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CCXXIV.—*The Preparation and Properties of Selenophen and Certain Halogen Derivatives of Selenophen.*

By Henry Vincent Aird Briscoe and John Buttery Peel.

Although the analogy between sulphur and selenium is well defined and thiophen is an interesting and important compound, its selenium analogue, *selenophen*, has hitherto been unknown to chemists. Relatively complex derivatives of selenophen, such as dimethylselenophen (Paal, *Ber.*, 1885, **18**, 2255), have been described and one investigator (Foa, *Gazzetta*, 1909, **39**, ii, 527) has stated that selenophen is obtained in small yield by heating together sodium succinate and phosphorus triselenide; but the product of this reaction, described as an unstable yellow liqnid, b. p. 147—149°/250 mm., and but slightly soluble in alcohol, differs so seriously from the substance we have prepared (*vide infra*) as to lead us to believe that Foa's observations are untrustworthy.

During attempts to prepare certain simple selenium compounds we found that the action of acetylene upon selenium at moderately high temperatures produced a mixture of substances, liquid at the ordinary temperature, from which selenophen could be isolated. The present communication describes the preparation of selenophen and records data for its b. p., m. p., density, thermal expansion, vapour density, molecular weight, surface tension, and refractive index, its salient chemical properties, and the preparation and properties of tetrabromoselenophen and tetrachloroselenophen.

The Preparation and Identification of Selenophen.—Although the action of acetylene on selenium has not previously been investigated, there are references in the literature to the analogous action of acetylene on sulphur. Meyer and Sandmeyer (*Ber.*, 1883, **16**, 2176) have reported that thiophen is thus produced, and Capelle (*Bull. Soc. chim.*, 1908, **4**, 150) states that the product is thiophten. Work now in progress in these laboratories, however, affords conclusive proof that appreciable quantities of thiophen can be produced from acetylene and sulphur.

The reaction between acetylene and selenium was carried out in a silica tube 22″ long and of 1½″ bore, heated over a length of 9″ by a suitable winding of nichrome wire lagged with alundum cement and asbestos millboard. The tube was slightly inclined and a glass adapter at the lower end led the volatile products into a vertical test-tube immersed in a cooling bath, whence uncondensed gases were led by a tube to the flue. Selenium, in lots of about 10 g., contained in a large porcelain boat, was placed in the heated portion

of the tube, the temperature being held at about 400° by adjustment of a rheostat in series with the furnace winding. Acetylene, taken from a cylinder of dissolved acetylene, was led through concentrated sulphuric acid in a bubbler and a drying-tube charged with phosphoric oxide, into the upper end of the furnace tube. At first no evidence of reaction was perceived, but after several hours hydrogen selenide was evolved and a dark brown oil began to condense in the receiver: in 24 hours about 15 c.c. of the oil were obtained. The tube, when opened, contained a black solid deposit at the lower end and, as in subsequent experiments the production of the brown oil began as soon as the tube attained the proper temperature, it seems probable that its formation is catalytically assisted by the black deposit. This point, however, is obscure.

A quantity of the brown oil, collected in a series of experiments, was fractionally distilled at a pressure of about 30—40 mm. and yielded the following fractions:

(i) A yellow liquid, collected up to 90°.
(ii) A yellow solid, collected at 95—135°.
(iii) A yellow-brown liquid, collected at 135—200°.
(iv) A dark brown residue.

Fraction (ii), after several recrystallisations from hot methyl alcohol, was white and proved to be naphthalene, m. p. 79·5°, mixed m. p. with naphthalene 80°. By a series of fractional distillations and crystallisations other solid products were obtained from the residues of fraction (ii) and fractions (iii) and (iv), among them anthracene, phenanthrene, and a bright yellow crystalline solid, m. p. 124°, which was probably either stilbene or distyrene. None of the higher fractions contained more than traces of selenium.

The low-boiling liquid, fraction (i), burned in an open dish with a bluish-white flame, a considerable amount of selenium being deposited. It was therefore submitted to a systematic fractional distillation at atmospheric pressure. In the first distillation, using an 18″ glass spiral column, the first fraction, collected between 79—90°, contained only a trace of selenium and consisted largely of benzene, but the greater part distilled between 104—110° and was evidently a selenium compound. This was twice fractionated, a well-lagged 48″ column packed with 4 mm. cylindrical glass beads being used, and yielded a final main fraction, b. p. 109·9—110·1°/752·1 mm. The liquid was finally purified by fractional solidification; it was thrice frozen partially in a bath of alcohol cooled with solid carbon dioxide, and the liquid portions were rejected. About 15% of the original oil was thus obtained as a pale lemon-yellow liquid, f. p. −38°, mobile, dense, and highly [illegible]

having a slight odour, not unpleasant, resembling both that of carbon disulphide and that of benzene: it burned in air with a bright blue flame, from which selenium was deposited on a cold surface. Subsequent experiments showed that the yellow colour was due to a minute trace of impurity, and that the liquid was really colourless.

To estimate selenium in the product, it was oxidised with concentrated nitric acid in a sealed tube at 200°, the contents of the tube were evaporated with excess of concentrated hydrochloric acid, the solution was boiled with sulphurous acid, and the precipitated elementary selenium was collected and weighed in the usual way. This method gives poor results but is the only one available. Carbon and hydrogen were determined by combustion in the usual way in a tube packed with copper oxide and lead chromate (Found: Se, 59·4, 58·2; C, 37·1, 37·5; H, 3·3, 3·3. C_4H_4Se requires Se, 60·3; C, 36·6; H, 3·05%).

The vapour density of the substance was determined by the Dumas method with a glass bulb heated in liquid paraffin or glycerol:

Temperature	140°	150°	200°
Barometric pressure (mm. Hg)	737·6	760·0	760·1
Volume of bulb (c.c.)	139·28	174·04	135·84
Weight of selenophen (g.)	0·5341	0·6710	0·4659
Molecular weight	133·9	134·0	133·0

The calculated value for C_4H_4Se is 131·2. The V.D. determinations were confirmed by two cryoscopic determinations of the molecular weight in benzene and bromoform. The former value is a little high, probably because a solid solution of selenophen in benzene crystallises out.

	Benzene as solvent.	Bromoform as solvent.
Weight of selenophen (g.)	0·4948	0·8282
Weight of solvent (g.)	17·91	56·80
Depression of freezing point	0·900°	1·580°
Molecular weight	156·0	132·2

The Physical Properties of Selenophen.—Using the Hofmann apparatus, with water in the jacket, determinations of the vapour pressure of selenophen were made over the range 25—85° and are recorded in Table I.

TABLE I.

Temp.	25°	30°	35°	38°	40°	43°	45°
Vap. press. (mm. Hg. at 0°)	46·5	55	66	74	78·5	87	94
Temp.	48°	50°	55°	58°	60°	65°	68°
Vap. press. (mm. Hg. at 0°)	104	112	131	146	156·5	185·5	206
Temp.	70°	73°	75°	77°	80°	83°	85°
Vap. press. (mm. Hg. at 0°)	221	243	259	277	305·5	335·5	356

Fig. 1 gives the vapour-pressure curve derived from these data and also the relationship of log P–T^{-1}, which is substantially linear.

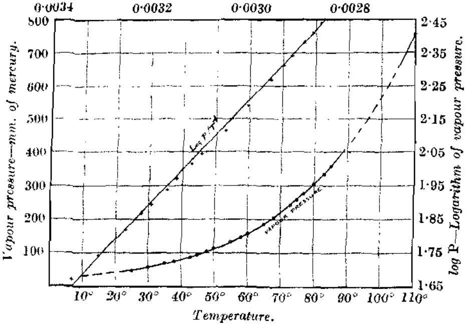
The latter curve, extrapolated to 760 mm. pressure, gives a value (108°) for the boiling point in reasonable agreement with that observed in the distillation of selenophen.

Determinations of density were made over the range 15—50° in glass Sprengel pyknometers of 10 c.c. capacity, fitted with ground glass stoppers and weighed against a tare. At each temperature of observation the pyknometer was filled with water and weighed and then filled with selenophen and weighed, the densities of selenophen and water at each of the six selected temperatures thus being directly compared. The data, recorded in Table II, show that the

Fig. 1.

Vapour pressure of selenophen.

1/T—Reciprocal of absolute temperature.



coefficient of expansion of the liquid is 3α (15—30°) = 0·001040, 3α (30—50°) = 0·001040, and 3α (15—50°) = 0·001045.

TABLE II.

Temp.	15·00°	20·00°	25·00°	30·00°	40·00°	50·00°
Density (g./c.c.)......	1·5307	1·5232	1·5156	1·5078	1·4943	1·4763

The refractive index $(n_D^{15^\circ})$ determined with a Pulfrich refractometer was 1·568.

The surface tension of selenophen was determined by Sugden's method, two especially good capillaries, calibrated by Dr. Robinson and Mr. Mills and kindly lent by them for this purpose, being used.

The radii of the tubes being respectively 0·25287 mm. and 0·49920 mm., the following data were obtained :

Temperature	15°	20°	25°
Difference in capillary rise (mm.)	9·56	9·44	9·30
Surface tension (dynes/cm.)	36·49	35·83	35·14
Parachor ($\gamma^{\frac{1}{4}}M/D$)	210·6	210·8	210·5

Dr. Sugden has very kindly made check determinations of the parachor, with the following results :

Temperature	17·5°	28·5°	33·5°	42°
D (g./c.c.)	1·501	1·485	1·476	1·464
γ (dynes/cm.)	35·63	34·28	33·31	32·32
Parachor	213·8	213·9	213·7	213·8

Unfortunately the sample of selenophen available for his measurements was less highly purified than that we had used : nevertheless his data serve to confirm the general nature of our results.

In the Eötvös–Ramsay–Shields' equation $(M/d)^{2/3}\gamma = K(T_c - T_0)$ the value of K is about 2·1, which may be held either to confirm the molecular weight deduced above or to show that selenophen is a " normal " liquid.

Assuming selenophen to have the constitution $\begin{matrix}CH{:}CH\\ CH{:}CH\end{matrix}\!\!>\!Se$, by deducting from its observed parachor (210·5), 4·8 for 4C, 17·1 for 4H, 23·2 for two double bonds, and 8·5 for one five-membered ring (total 142·5), we obtain for selenium the parachor 68·0. This value is in fair agreement with the value 64 obtained by Dr. Sugden (private communication) in a study of several other selenium compounds.

Chemical Properties of Selenophen.—Selenophen is insoluble in water, but is miscible in all proportions with a number of non-aqueous liquids, including acetone, benzene, and carbon disulphide. At its boiling point it dissolves sulphur quite readily. It closely resembles thiophen in its remarkable stability and chemical inactivity. It is unaffected by boiling with water, caustic soda solution or concentrated hydrochloric acid. It does not form a picrate and yields no methiodide even when treated with methyl iodide in a sealed tube at 160° for 24 hours. It has but a very slight reducing action on potassium permanganate in acetone solution and when distilled from the unchanged permanganate and fractionated to remove acetone, practically the whole of the selenophen taken is recovered, but as a *colourless* liquid. Evidently the only effect of the permanganate is to oxidise the small trace of impurity, probably a hydrocarbon, responsible for the slight yellow colour of the distilled and crystallised selenophen.

Selenophen is not reduced by the ordinary agents, such as zinc

and hydrochloric acid, and it is recovered practically unchanged after thrice being passed together with hydrogen at 250° over nickel (on pumice; obtained by heating the sulphate in a current of hydrogen at 400° for 24 hours).

Selenophen reacts with concentrated sulphuric acid with the production of a greenish-black mass; when warmed with concentrated sulphuric acid and isatin, it gives an indophenin reaction characterised by a greenish-blue colour, becoming purple when the product is poured into water. When concentrated sulphuric acid was added cautiously to a solution of selenophen in acetic anhydride well cooled in ice and the product was poured into water, a brown, semi-solid substance was obtained which may possibly have been a sulphonic derivative. It was, however, insoluble in water and the common organic solvents and decomposed on heating. Further attempts are being made to investigate the product.

Difficulties also attended attempts to prepare nitro-derivatives of selenophen. It was vigorously oxidised by concentrated nitric acid, but when solutions of selenophen and of concentrated nitric acid in acetic anhydride were slowly mixed in the cold, and the product was poured into ice-cold water, a dark brown oil separated which slowly set to a brown tar. This tar had the characteristic smell of nitro-compounds and dissolved readily in aqueous caustic soda to give a red solution, but it was insoluble in water, ether, light petroleum, benzene, alcohol, carbon tetrachloride, ethyl acetate, or acetic acid and so its investigation was deferred.

Tetrabromoselenophen.—A vigorous reaction occurred and hydrogen bromide was evolved when a solution of bromine in carbon disulphide, slightly in excess of the calculated amount, was added to a well-cooled solution of selenophen (10 g.) in the same solvent. After 24 hours, the solution was washed with dilute caustic soda solution and with water and evaporated on the water-bath. The brown residue, on recrystallisation from alcohol, gave *tetrabromoselenophen* as a white, finely crystalline substance, m. p. 102° (yield, about 70%). Tetrabromoselenophen is stable at its m. p., and does not reduce permanganate in acetone solution, but on boiling with water it slowly decomposes and deposits selenium.

Bromine and selenium were estimated in the compound by oxidising it with nitric acid and silver nitrate in a sealed tube at 200°, and boiling the silver bromide with dilute nitric acid to dissolve any silver selenite present. The silver bromide was dried, and weighed, and selenium was estimated in the filtrate by precipitation as the element in the usual way after the excess of silver had been removed as silver chloride (Found: C, 11·2, 11·1; Br, 71·5, 71·3; Se, 15·7, 17·7; *M*, cryoscopic in benzene, 565, 541. C_4Br_4Se requires C, 10·7;

Br, 71·4; Se, 17·9%; *M*, 447·2). Hence the compound appears to have the simple molecular formula, but probably forms solid solutions with benzene.

Attempts to isolate a corresponding iodine derivative by similar methods have failed.

Tetrachloroselenophen.—On adding a slight excess of a saturated solution of chlorine in carbon disulphide to a solution of selenophen (10 g.) in the same solvent, reaction occurred and hydrogen chloride was evolved. After 2 days the solution deposited a pale yellow, crystalline solid, which appeared to be insoluble in most solvents and steadily evolved hydrogen chloride on keeping. A similar product, prepared by bubbling gaseous chlorine slowly through a carbon disulphide solution of selenophen (10 g.), when washed well with water and dried on a porous plate, was sufficiently soluble in toluene to be recrystallised from that solvent and the product was a finely crystalline, white solid (Found: C, 16·9; Cl, 53·5; Se, 30·5. C_4Cl_4Se requires C, 17·7; Cl, 52·6; Se, 29·6%).

The yield in this case was only about 25%, and the mother-liquor contained other selenium compounds, which are being investigated. When heated to 87°, the solid decomposes, evolving an acid gas, and fuses to a yellow liquid that does not resolidify. A similar decomposition appears to occur in toluene or alcohol solutions, which, if overheated, become yellow and thereafter do not, on cooling, deposit crystals.

The compound was not soluble in a solvent of convenient freezing point, and so its molecular weight was not determined.

Although the analysis given appears to show that the compound is tetrachloroselenophen, it differs from tetrabromoselenophen to a rather remarkable extent. Unlike the latter, it is easily decomposed, with deposition of selenium, on warming with water or with acids, and slowly decomposes at the ordinary temperature, in air in a closed tube or in a vacuum, evolving acid fumes and turning brown. These differences suggest some difference in chemical character between the two halogen derivatives, and this is the subject of further inquiry.

Acknowledgment is made of a grant from the Research Fund Committee of Armstrong College, which enabled one of us (J. B. P.) to take part in this investigation.

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CCXXV.—*Studies of Valency. Part IX. Molecular Structure of Thallium Salts.* (a) *Thallium Tri-iodide;* (b) *Alkyl Derivatives.*

By Arthur John Berry and Thomas Martin Lowry.

(*a*) *Thallium Tri-iodide* [with Mrs. R. R. Goldstein].

Thallium tri-iodide may be formulated either as thallic iodide or as a thallous polyiodide. From analogy with other thallic salts, the first of these formulæ has been generally adopted; but, since the iodide is a black, insoluble compound, whilst thallic chloride and bromide are soluble deliquescent salts, there is ample contrast to justify a different formulation of the iodide. Thus, Wells and Penfield (*Z. anorg. Chem.*, 1894, **6**, 312) concluded that, since thallium tri-iodide is isomorphous with the tri-iodides of rubidium and cæsium, it should be formulated as the polyiodide of a univalent metal. The formation of a polyiodide by thallium would be exceptional, however, since the ease of formation of polyiodides increases with the atomic volume of the kation (Ephraim, "Inorganic Chemistry," 1926, p. 200), reaching a maximum in the case of cæsium, with atomic volume 70, whereas the atomic volume of thallium (17) lies between those of lithium (13) and sodium (23·7). Maitland and Abegg (*Z. anorg. Chem.*, 1906, **49**, 341), on the other hand, suggested that thallium tri-iodide may be tautomeric, exhibiting one or other structure according to the reagent employed. Thus the sparing solubility of the iodide is cited as characteristic of a thallous salt, whilst the capacity of forming complex ions, as in the compound $KTlI_4$, which Johnson prepared in 1878 from potassium tri-iodide and thallous iodide (J., **33**, 183), is characteristic of thallic salts.

This conflict of opinion has been resolved in the present paper with the help of spectroscopic observations, which show that the iodine in alcoholic solutions of thallium tri-iodide is not present in the form of a tri-iodide ion. Spectroscopic observations have also shown that, although thallium tri-iodide does not combine with iodine to form a pentaiodide $[TlI_2]I_3$, the complex salt $KTlI_4$ persists in solution. Several new addition compounds of thallium tri-iodide with pyridine and with the chloropyridines are also described, which retain their individuality in solution. The spectroscopic evidence, which shows that the trihalides are not ionised completely even in dilute solutions, has been corroborated by measurements of conductivities in methyl alcohol and in acetonitrile, which show that the trihalides behave only as weak binary electrolytes. Finally, it has been shown that the chemical properties of

thallium tri-iodide and of its compounds with pyridine are those of a *thallic* salt, giving only doubtful indications of thallous ions in solution.

Chemical Properties.—Well-formed crystals of thallium tri-iodide were prepared by boiling thallous iodide and iodine in equivalent proportions with methyl alcohol in a reflux apparatus, filtering the liquid, and concentrating it by evaporation in a vacuum desiccator containing calcium chloride. When titrated with potassium iodate in presence of a high concentration of hydrochloric acid (Berry, *Analyst*, 1926, 137), 0·261 g. of the crystals gave a titre corresponding with 0·264 g. of TlI_3. Reduction by heating with excess of sodium arsenite solution gave 56·0% of TlI (TlI_3 requires 56·6%). 0·293 G. of the compound gave 0·353 g. of silver iodide, whence I = 65·1% (Calc., 65·1%).

The brown solutions of thallium tri-iodide in alcohol, acetone, acetonitrile, and nitrobenzene show the reactions of tervalent thallium but only give doubtful indications of the presence of thallous ions. Thus, when excess of alkali is added to solutions of thallium tri-iodide in methyl alcohol or in acetonitrile, a quantitative yield of thallic oxide is produced, *e.g.*, 0·5355 g. of the iodide in acetonitrile gave 0·206 g. of oxide, the calculated yield being 0·209 g. On the other hand, when potassium bromide or iodide in aqueous acetonitrile is added to a solution of thallium tri-iodide in acetonitrile, a slight turbidity is produced, which might be attributed to the separation of thallous bromide or iodide; but this disappears on the addition of an excess of the alkali halide, and no turbidity was observed when methyl alcohol was used as solvent in place of acetonitrile. Again, when potassium chromate in aqueous acetonitrile is added to a solution of thallium tri-iodide in acetonitrile, a little thallous chromate separates; but when methyl alcohol is used as a solvent a precipitate of thallic hydroxide is produced.

When aqueous potassium iodide is added to solutions of thallium tri-iodide, the colour becomes paler, and precipitation of thallic oxide is impeded. Thus, whilst sodium hydroxide gives a precipitate immediately, sodium carbonate does so only after a few moments, unless the liquid is heated. Ammonia precipitates thallic oxide, but precipitation is prevented if ammonium chloride be first added. Since these phenomena appear to be due to the formation of complex ions, experiments were made on the behaviour of aqueous potassium iodide towards thallium tri-iodide dissolved in nitrobenzene. It was found that rather less than one molecular proportion of potassium iodide was taken up by thallium tri-iodide in the nitrobenzene solution.

Reducing agents convert thallium tri-iodide into thallous iodide,

but no conclusions can be drawn regarding the constitution of this compound by considering its response to reagents such as sodium arsenite and thiosulphate, since other thallic salts are reduced by them and both reagents are oxidised by tri-iodide ions.

Preparation of Derivatives of Thallium Tri-iodide with Pyridine and with Chloropyridines.—Meyer (*Z. anorg. Chem.*, 1900, **24**, 321) prepared addition compounds by adding pyridine to aqueous solutions of thallic chloride or bromide; these compounds are white, sparingly soluble substances, which are readily hydrolysed by water with separation of thallic oxide. If, however, pyridine be added to solutions of thallic chloride containing excess of hydrochloric acid, the product contains thallium and chlorine in the ratio of 1 to 4. Addition compounds of thallic iodide with pyridine were prepared by Renz (*Ber.*, 1902, **35**, 1110), who described the compound TlI_3,C_5H_5N as a "dunkel orangerothes krystallinisches Pulver" and the compound $(TlI_3)_2(C_5H_5N,HI)_3$ as a "prächtig zinnoberrothes krystallinisches Pulver." The percentages of thallium in these products were not determined, but those of the other elements were in agreement with the formulæ assigned. Our own observations are set out below.

(*a*) *Pyridinium iodide.* When pyridine is added to solutions of thallium tri-iodide, fine orange-coloured precipitates are formed. Darker-coloured compounds were obtained when the base was added to solutions prepared by dissolving thallic oxide in aqueous hydriodic acid, or to solutions of thallium tri-iodide containing excess of iodine in organic solvents, but since the ratio of thallium to iodine varied from 1/3 to 1/5, it is very doubtful if any of these preparations was pure. One specimen, which separated from acetone in fine, dark red crystals, gave, however, a ratio Tl : I = 1 : 4 exactly, with two molecular proportions of pyridine to each atom of thallium, and therefore appeared to be a definite chemical *compound*.

(i) The compound was reduced with sodium arsenite, the resulting thallous iodide collected and weighed (TlI = 40·2%), and the filtrate analysed by Volhard's method (43·6% of additional iodine), *i.e.*, Tl = 24·8%, I = 59·0%; the pyridine is therefore 16·2% (by difference). (ii) The compound was reduced by sodium arsenite, the resulting thallous iodide being determined by direct titration with potassium iodate (Found: TlI, 39·3%; *i.e.*, Tl = 24·2%). (iii) By gravimetric analysis, I = 58·0% [$(C_5H_5N)_2HTlI_4$ requires Tl, 23·4; I, 58·4; C_5H_5N, 18·2%].

(*b*) *Pyridine.* By grinding pure thallium tri-iodide with a considerable excess of pyridine, a *compound* having the composition $(C_5H_5N)_2TlI_3$ was readily prepared. After filtration from a small insoluble residue, the liquid was largely diluted with water; the

orange-coloured precipitate was collected, and dried over soda-lime in a desiccator. Two such preparations were analysed (i) by titration with potassium iodate directly, and (ii) by titration with potassium iodate of the thallous iodide obtained by reduction with sodium arsenite [Found: TlI, 43·8, 44·1; I (extra), 33·8, 34·5; C_5H_5N (by diff.), 22·4, 21·4; I (total, as AgI), 50·7. $TlI_3(C_5H_5N)_2$ requires TlI, 44·5; I (extra), 34·2; C_5H_5N, 21·3; I (total), 51·3%].

This addition compound dissolves readily in many organic solvents, forming coloured solutions; but whilst iodine is violet in chloroform or benzene, and brown in alcohol or acetone, solutions of the compound of thallium tri-iodide and pyridine have the same golden-yellow colour in methyl and ethyl alcohol, acetone, glacial acetic acid, benzene, nitrobenzene, or nitromethane. Moreover, when pyridine is added to a solution of thallium tri-iodide in acetonitrile, the dark brown colour is changed to a pale golden-yellow. The chemical reactions of the tri-iodide do not, however, appear to be modified by the presence of pyridine.

(c) *Dichloropyridine.* A *compound* was prepared by boiling thallium tri-iodide (3 g.) and dichloropyridine (4 g.) with methyl alcohol for 2 hours under reflux. The dark brown liquid was decanted from some undissolved thallium tri-iodide, and the compound was precipitated by dilution with water. The golden-yellow, crystalline solid was collected and dried by exposure over soda-lime in a desiccator. Analysis of two samples gave TlI, 25·0, 25·1; I (extra), 19·6, 19·8; $C_5H_3NCl_2$ (by diff.), 55·4, 55·1. $TlI_3(C_5H_3NCl_2)_5$ requires TlI, 25·0; I (extra), 19·2; $C_5H_3NCl_2$, 55·8%.

(d) *Trichloropyridine.* When this was boiled with thallium tri-iodide in methyl-alcoholic solution, a *compound* was isolated as before [Found: TlI_3, 37·8. $TlI_3(C_5H_2NCl_3)_5$ requires TlI_3, 39·1%].

(e) *Tetrachloropyridine* combines only slowly with thallium tri-iodide. On addition of excess of water to the alcoholic solution, a yellow precipitate separates, but it soon decomposes with separation of thallous iodide and free iodine. The successive replacement of hydrogen by chlorine in the pyridine nucleus appears to diminish the basic properties to such an extent as to prevent the formation of stable additive compounds.

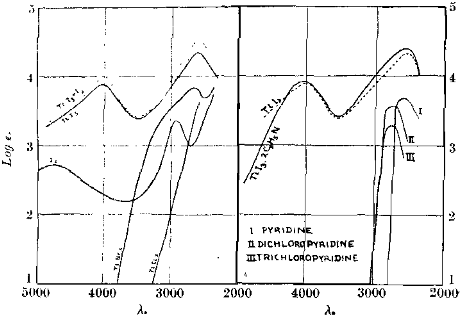
(f) *Pentachloropyridine* did not give an addition compound with thallium tri-iodide.

Absorption Spectra.

The extinction coefficients were determined in absolute methyl alcohol (free from acetone) by methods which have already been described. The iodide was dissolved directly in the solvent by vigorous stirring, but the chloride and bromide, which are very hygroscopic, were extracted with methyl alcohol from the yellow

double salts, $TlCl_3,3TlCl$ and $TlBr_3,TlBr$ (Berry, *Proc. Camb. Phil. Soc.*, 1924, **22**, 363), and the thallium content was determined by analysis. The complex salt, $KTlI_4$, was prepared in blackish-brown crystals by refluxing thallium tri-iodide and potassium iodide with alcohol and allowing the solution to evaporate in a desiccator containing calcium chloride; the alcohol-wet crystals were dissolved in methyl alcohol and the thallium content of the solution was

FIG. 1. FIG. 2.



Molecular extinction coefficient of $TlCl_3$, $TlBr_3$, *and* TlI_3 *in methyl alcohol.*

Molecular extinction coefficients of pyridine compounds in methyl alcohol.

determined by analysis. The extinction coefficients have been plotted in Figs. 1, 2, and 3, and the most important data are summarised in Table I.

TABLE I.

Extinction Coefficients of Tervalent Compounds of Thallium.

Formula.	Logarithm of extinction coefficient.		
$TlCl_3$	1·0 at 3240	3·0 at 2740	
$TlCl_3(C_5H_5N)_2$	1·0 at 3200	3·0 at 2780	
	Maxima.		Step-out.
$TlBr_3$	3·85 at 2670		
TlI_3	3·9 at 4000	4·35 at 2600	
$TlI_3 + I_2$	4·0 at 4000	4·45 at 2550	4·2 at 2900 to 2700
$TlI_3 + KI$	3·9 at 4000	Not observed	4·0 at 2950 to 2750
$KTlI_4$	4·0 at 4020	4·45 at 2550	4·05 at 3000 to 2800
C_5H_5N		3·65 at 2590	
$C_5H_3NCl_2$		3·55 at 2710	
$C_5H_2NCl_3$		3·40 at 2760	
$TlI_3 + (C_5H_5N)_2$ ...	3·9 at 4010	4·4 at 2600	
$TlI_3,(C_5H_3NCl_2)_5$ ...	3·9 at 4000	4·4 at 2630	
$TlI_3,(C_5H_2NCl_3)_5$ ...	3·8 at 4000	4·4 at 2630	
$HTlI_4,(C_5H_5N)_2$ ...	4·0 at 4030	4·45 at 2580	4·0 at 3000 to 2750

The absorption spectra of $TlCl_3$, $TlBr_3$, and TlI_3 may be compared either with those of $CHCl_3$, $CHBr_3$, and CHI_3 (J., 1926, 622) or with those of KCl, KBr_3, and KI_3 (*loc. cit.*). In each series the chloride shows only a general absorption in the far ultra-violet region, whilst the bromides show at least the close proximity of an absorption band; the iodides, on the other hand, give two absorption bands, one in the more distant part of the ultra-violet spectrum, and the other with its foot extending into the visible spectrum and giving rise to visible colour. *This produces a contrast between the black* tri-iodide and the colourless trichloride which is sufficient to prove that the thallic salts are not mere aggregates of thallium and halogen ions, as the corresponding thallous salts appear to be. On the other hand, the fact that the two maxima in TlI_3 are separated by 1400 Å.U., whereas the maxima given by $\overset{+}{K}\overset{-}{I_3}$ and by $C_6H_4Br{\cdot}\overset{+}{N}Me_3\overset{-}{I_3}$ (unpublished measurements) are only separated by 650 and 720 Å.U., respectively, is incompatible with the view that the absorption is caused by a tri-iodide ion. The absorption curves also show that, whereas the tri-iodide ion produces a "general absorption" beyond the twin maxima, the molecular extinction coefficients of thallium tri-iodide decrease progressively at wave-lengths less than those of the two maxima. We therefore conclude that the iodine atoms are not present as a tri-iodide ion, but are joined, at least in part, by covalent bonds directly to the metal. This conclusion is obviously compatible with the view that, since the tri-iodide does not differ from the double salts $Tl_3^{I}(TlCl_6)$, $Tl_3^{I}(TlBr_6)$, and $Tl^{I}(TlBr_4)$ in the same pronounced way as from the simple chloride and bromide, the *solid iodide may perhaps be a double salt,* $Tl^{III}(TlI_6)$, *of the cryolite* type; but the data now recorded do not enable us to test the validity of this very plausible view.

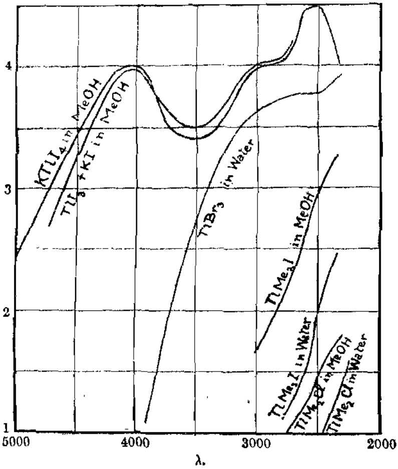
A study of the absorption spectra provides a similar solution to the similar problem presented by the tribromide. Since it gives an ultra-violet absorption band ($\log \varepsilon = 3{\cdot}85$ at 2670 Å.U.) which is not given either by thallic chloride or by potassium bromide, we can again conclude that the salt is not a mere aggregate of thallium and halogen ions; on the other hand, the bromine cannot be present as a perbromide ion, since the details of the absorption spectra differ very widely, in spite of a superficial resemblance between the maxima set out below:

$\overset{+}{K}\overset{-}{Br_3}$	Maximum	at $\log \epsilon = 3{\cdot}5$ at 2700 Å.U. in water.
$C_6H_4Br{\cdot}\overset{+}{N}Me_3\overset{-}{Br_3}$	,,	at $\log \epsilon = 3{\cdot}4$ at 2600 Å.U. in alcohol.
$TlBr_3$	,,	at $\log \epsilon = 3{\cdot}85$ at 2670 Å.U. in methyl alcohol.

Thus the two perbromides give a narrow absorption band at 2600—

2700 Å.U., but this is preceded by a well-marked step-out, which only just fails to reach a maximum, log ε = 1·8 at λ = 3800, just beyond the visible region of the spectrum. Thallium tribromide, on the other hand, gives a broad unsymmetrical maximum at 2670 Å.U., but with no sign of a step-out at 3800 Å.U., since the solutions are highly transparent in the part of the spectrum where the two perbromides only just fail to give an absorption band. The data

FIG. 3.



Molecular extinction coefficients of potassium thallic iodide, etc.

for an *aqueous* solution of thallium tribromide, which are reproduced in Fig. 3, are almost identical with those for the solution in *methyl alcohol* in Fig. 1, but show a step-out in place of the shallow maximum.

In the case of the trichloride no similar question arises, since the trichloride ion appears to be still unknown; and the "general absorption" of the salt is in complete agreement with this conclusion.

In addition to the simple salts, an equimolecular mixture of thallium tri-iodide and iodine was examined, in order to ascertain

whether one of the atoms of iodine could be converted into a tri-iodide ion; but the mixture gave only an additive absorption, including the two maxima of thallium tri-iodide and a step-out at 2900 Å.U. A similar step-out is found in the spectrum of the complex salt $KTlI_4$, solutions of which were prepared both by dissolving the black crystals of the salt and by mixing potassium and thallic iodides. Since potassium tri-iodide gives a band at 2900 Å.U., this step-out might be attributed to a reversible formation of potassium tri-iodide, according to the equation

$$KI + TlI_3 \rightleftharpoons KTlI_4 \rightleftharpoons KI_3 + TlI;$$

but this would not be in harmony with the conclusions of Maitland and Abegg as to the stability of the $[TlI_4]^-$ ion.

The addition compounds of thallium tri-iodide with pyridine and with the chloropyridines have lost the black colour of the tri-iodide, and show instead various shades of orange-red; the pyridinium compound, $(C_5H_5N)_2HTlI_4$, is also bright red. These changes of colour are due to alterations in the foot of an absorption band on the edge of the visible region, the width of which is greatly reduced when the tri-iodide is combined with pyridine, but they are not accompanied by any marked changes in the ultra-violet absorption of the salt.

Molecular Conductivities.

The conductivities of the trihalides were measured by methods that have already been described. Since thallium tri-iodide is insoluble in water, the solvents used were methyl alcohol and acetonitrile. The methyl alcohol was refluxed for 3 hours with sodium hydroxide, fractionated, and then treated with a mercury–aluminium couple until no further action took place. Basic impurities, such as methylamine, were eliminated by distillation from succinic acid, after which the product was dried again with a fresh mercury–aluminium couple; the alcohol was then dry enough to permit of the use of phosphoric oxide for further desiccation. The acetonitrile, from Messrs. British Drug Houses, had an initial conductivity of 35 gemmho. It was allowed to stand over solid potassium hydroxide for several hours to remove acetic acid and moisture, and was then dried with calcium chloride, distilled, shaken with a little phosphoric oxide for several hours, and left in contact with it over-night. After a final distillation the specific conductivity of the liquid had fallen to 1·9 gemmho.

Thallic chloride and bromide were extracted from the double salts, $TlCl_3,3TlCl$ and $TlBr_3,TlBr$ or $TlBr_3,3TlBr$, by prolonged contact with the solvent, and were separated from the thallous

halides by filtration. Since the thallous halides dissolve to an appreciable extent in acetonitrile *in the presence of the thallic halides*, a definite source of error remains, even when the conductivities of the saturated solutions of the two thallous salts (6·037 gemmho for the chloride and 9·781 gemmho for the bromide) are deducted from the values obtained for the corresponding thallic salts. This source of error becomes inappreciable, however, when methyl alcohol is used as the solvent, and is absent in the case of the iodide, which was weighed out and dissolved directly in the solvent.

TABLE II.

(i) *Molecular Conductivities of Thallium Salts in Acetonitrile at 25°.*

(*a*) Thallium trichloride (filtered from thallous chloride).

v =	*56*	*112*	*224*	*448*	*896*	*1792*	*3584*		
$\Lambda^{25°}$ =	129	139	148	154	161	161	169		

(*b*) Thallium tribromide (filtered from thallous bromide).

v =	*5*	*11*	*22*	*43*	*86*	*171*	*343*	*686*	*1371*
$\Lambda^{25°}$ =	80	89	98	106	113	120	125	129	134

(*c*) Thallium tri-iodide.

v =	128	256	512	1024	2048	4096
$\Lambda^{25°}$ =	79	85	91	99	109	116

(*d*) Tetraethylammonium iodide (Walden).

v =	100	200	500	800	1000	2000	4000	8000	∞
$\Lambda^{25°}$ =	*142*	*163*	*173*	*175*	*180*	*184*	*186*	*189*	*200*

(ii) *Molecular Conductivities of Thallium Salts in Methyl Alcohol at 25°.*

(*a*) Thallium trichloride (filtered from thallous chloride).

v =	*101*	*202*	*404*	*808*	*1616*
$\Lambda^{25°}$ =	28	30	31	33	36

(*b*) Thallium tri-iodide.

v =	*128*	*256*	*572*	*1024*	*2048*
$\Lambda^{25°}$ =	17	20	24	29	39

(*c*) Dimethylthallonium iodide.

v =	141	256	512	1024	2048
$\Lambda^{25°}$ =	62	69·7	78	85	90·5

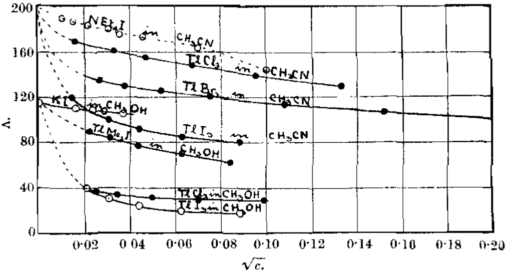
(*d*) Potassium iodide (Frazer and Hartley).

v =	721	1243	1724	2346	3997	∞
$\Lambda^{25°}$ =	*105·16*	*107·45*	*108·57*	*109·44*	*110·73*	*114·85*

The molecular conductivities of the trihalides are shown in Table II, where some other typical data are included for comparison; but the only results from which quantitative conclusions can be drawn are for the trichloride in methyl alcohol and for the tri-iodide in methyl alcohol and in acetonitrile. The conductivities in acetonitrile are several times greater than those of lithium chloride, and rather more than half as great as those of sodium or potassium iodide; but it is clear that the salts are behaving only as binary electrolytes, and that their electrolytic dissociation does not extend

beyond the first halogen $TlX_3 \rightleftharpoons TlX_2^+ + X^-$. A similar statement can be made in reference to the solutions in methyl alcohol, where the conductivities of the two thallium salts at a dilution of $N/2000$ are still only about one-third as great as those of potassium iodide. The conductivity data are therefore in agreement with the absorption spectra in indicating that, even in dilute alcoholic solutions, a part of the halogen is still attached to the metal. Moreover, since the curves obtained by plotting Λ against $\sqrt{c}$, as in Fig. 4, deviate very widely from the linear relation given by potassium iodide in methyl alcohol, and the inflected line for tetraethylammonium iodide in acetonitrile, it is clear that, even when the salts are regarded only as binary

FIG. 4.



Molecular conductivities of thallium salts in acetonitrile and in methyl alcohol.

electrolytes, their electrolytic dissociation is very much below that required for complete ionisation according to the formulæ of Debye and Hückel.

(*b*) *Alkyl Derivatives* [with F. L. GILBERT].

Although thallium forms many tervalent salts, the only alkyl derivatives that have been prepared up to the present are of the type $TlMe_2I$; moreover, these dialkyl halides cannot be condensed by the action of metallic sodium to molecules of the type $Me_2Tl{\cdot}TlMe_2$, comparable with the (bimolecular) lead trixylyl, $(C_8H_9)_3Pb{\cdot}Pb(C_8H_9)_3$, prepared by Krause and Smitz (*Ber.*, 1919, **52**, 2165). Since no convincing explanation has yet been given of the non-formation of tri-alkyl compounds of the type $TlMe_3$, it appeared desirable to investigate the dialkyl derivatives, in order to find out whether their ionisation is " complete," as in the case of the quaternary ammonium

bases and salts, or whether it is reversible and incomplete as in the case of ammonium hydroxide and mercuric chloride.

Dimethylthallonium iodide was prepared by the action of the Grignard reagent on the ether-soluble pyridine compound of thallic bromide, and the product was compared with a specimen generously placed at our disposal by Dr. Goddard, which had been prepared by a modification of the method of Meyer and Bertheim (*Ber.*, 1904, **37**, 2051). Our material had a salmon-pink tint, whilst Dr. Goddard's was tinted yellow, but in each case the colour was removed when the solutions were filtered; both specimens decomposed at 275°, although the decomposition point recorded by Goddard (J., 1921, **119**, 674) was 295°. We are also indebted to Dr. Goddard for preparations of the diethyl iodide, the dipropyl bromide and iodide, and the dibutyl bromide. These sparingly soluble salts were washed with water before being converted into the freely soluble bases, and in some cases the salts were recovered in a purified form by neutralising the base with a halogen acid.

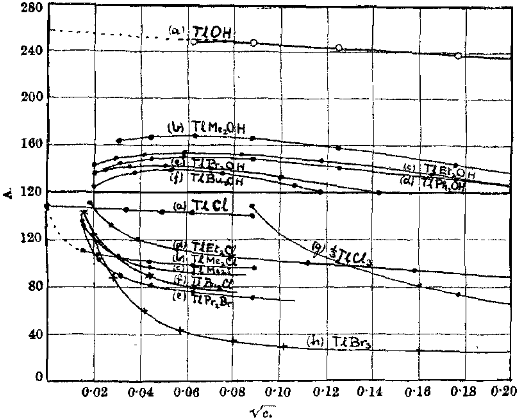
The experimental work included measurements of the molecular conductivity of aqueous solutions of several of the dialkyl halides, and of the bases from which they were derived, but comparative observations were also made of the conductivity of thallium tribromide in water. Potentiometric observations were made of the neutralisation of the dimethyl base with *N*-sulphuric acid and of the dipropyl base with *N*-hydrochloric acid; a comparative series of potentiometric measurements was also made of the neutralisation of thallous hydroxide with *N*-sulphuric acid. Finally, the molecular extinction coefficients of dimethylthallonium chloride and iodide were measured in aqueous and methyl-alcoholic solutions, as well as those of aqueous thallic bromide, which had been examined previously in methyl alcohol.

Molecular Conductivities.

(*a*) *Dialkyl Salts.*—The molecular conductivities of aqueous solutions of dimethylthallonium chloride and iodide are set out in Table III (*i*), with Shukoff's data for the diethyl chloride (*Ber.*, 1905, **38**, 2691), and our own data for the dipropyl bromide (decomposes without fusion at 240°), and for a specimen of the dibutyl chloride (decomposes without fusion at 160°), which we prepared through the free base from Dr. Goddard's specimen of the bromide; the molecular conductivities have also been plotted in Fig. 5 against the square root of the concentration. Ostwald's data for thallous chloride, which give an exactly linear relation between Λ and $\sqrt{c}$, were taken as a criterion of the behaviour of a binary salt which is ionised completely even in the solid state. It is then immediately

obvious that the molecular conductivity of the chloride, $TlMe_2Cl$, falls very far short of the standard for complete ionisation, although there is no clear evidence of hydrolysis, since the curve could be extrapolated quite easily to the value of Λ_∞ given by the data for thallous chloride.* *On the other hand, the molecular conductivity* of the iodide, $TlMe_2I$, rises so rapidly in dilute solutions that we are obliged to postulate an extensive hydrolysis of the salt, since extrapolation to zero concentration would give a value far in excess of the

FIG. 5.



Molecular conductivities of thallium bases and salts in water.

molecular conductivity of a binary electrolyte. Shukoff's data for diethylthallonium chloride, which were carried to much higher concentrations, show just the same phenomena of incomplete electrolytic dissociation in strong solutions and hydrolysis in weak solutions. The curve for the diethyl chloride is followed fairly closely by our own curve for the dibutyl chloride; the dipropyl bromide, on the other hand, appears to be even less completely dissociated, and more extensively hydrolysed, than the dibutyl

* The curve for the dimethyl chloride intersects the curves for other dialkyl halides, but its accuracy was confirmed by a duplicate series of measurements.

chloride, to which it is related in much the same way as the chloride and iodide of the dimethyl base.

(*b*) *Thallic Chloride and Bromide*.—Evidence of hydrolysis was also obtained on measuring the molecular conductivities of aqueous solutions of thallium tribromide. A solution was prepared by extracting the yellow tetrabromide, $Tl[TlBr_4]$, with water, and its concentration was estimated by gravimetric analysis. Since the thallous salt is insoluble in water, even in the presence of the thallic salt, the correction which was required for solutions in acetonitrile (p. 1756) is no longer needed. The results of the measurements are included in Table III (i), together with Meyer's data for the chloride (*Z. anorg. Chem.*, 1900, **24**, 341). Over the range from 19·4 to 1240 litres, the conductivities are independent of time, but are lower than those of a typical binary salt. At a dilution of 2480 litres, however, the increment of conductivity on doubling the volume, which had been growing progressively throughout, rose to nearly 50% in the freshly diluted solution, and a further increase of nearly 50% occurred when the solution was kept for an hour. This behaviour shows again that a part of the conductivity is due to hydrolysis, exactly as Meyer had postulated in the case of the chloride. The phenomena of incomplete electrolytic dissociation in concentrated solutions and extensive hydrolysis in dilute solutions are, indeed, even more strongly marked in thallic bromide (where the curve plotted in Fig. 5 turns suddenly vertical at $\sqrt{c} = 0{\cdot}02$) than in the alkylated salts. The curve for thallic chloride is of a similar type, but it is difficult to say whether the higher conductivity of the solutions is due to a higher degree of ionisation of the salt or merely to a more extensive hydrolysis.

It is perhaps desirable to add that the evidence cited by Meyer (*Z. anorg. Chem.*, 1900, **24**, 321; 1902, **32**, 72) to show that only two-thirds of the chlorine in thallic chloride is precipitated by silver nitrate has not been confirmed (Cushman, *Amer. Chem. J.*, 1901, **26**, 505) and cannot therefore be used as a proof that only a part of the halogen is ionisable. In our experience, there is a perceptible weakening of the opalescence when a very dilute solution of thallic chloride is mixed with silver nitrate and thallic nitrate is then added; but on keeping for some time the opalescence returns to its original strength. We also find that, just as in the case of ferric oxide, hydrochloric acid is a much better solvent for thallic hydroxide than is nitric acid, which only dissolves the oxide very slowly (Willm, *Ann. Chim. Phys.*, 1865, [4], **149**, 76). For this experiment, equal quantities of thallic hydroxide were precipitated from 1 g. each of the pyridine compound of thallic bromide; the precipitate was only partially dissolved even when heated with 50 c.c. of *N*-nitric acid,

but it was dissolved at once in the cold by only 5 c.c. of *N*-hydrochloric acid; and, when a brown cloud had been produced by diluting to 2000 c.c. and adding 1 c.c. of *N*-sodium carbonate, the liquid was rendered clear again by adding only 2 c.c. of *N*-hydrochloric acid. The incomplete ionisation of thallium tribromide can, however, be demonstrated by a qualitative experiment in the same way as in the case of mercuric chloride. For this purpose, a sample of thallic oxide, which gave no coloration when digested under identical conditions with aqueous phenolphthalein, was heated in a test-tube in a water-bath with aqueous potassium bromide and phenolphthalein, whereupon a very decided alkalinity appeared after a short time. A similar alkalinity was developed in aqueous potassium chloride. This result can be explained by assuming a fixation of bromide ions by the thallium, with a consequent liberation of hydroxyl ions as shown in the reversible equation:

$$Tl(OH)_3 + 3\overset{+}{K}\overset{-}{Br} \rightleftharpoons TlBr_3 + 3\overset{+}{K}\overset{-}{OH}.$$

TABLE III.

(i) *Molecular Conductivities of Thallium Salts in Water at 25°.*

(*a*) TlCl	v =	128	256	512	∞				
(Kohlrausch)	Λ^{25° =	*140*	*143*	*145*	*149*				
(*b*) $TlMe_2Cl$	v =	128	256	512	1024	2048	4096		
	Λ^{25° =	96	98	100	103	106	111		
		97	100	102	105	108	114		
(c) $TlMe_2I$	v =	256	512	1024	2048	4096			
	Λ^{25° =	93	97½	104	118	131			
(*d*) $TlEt_2C$	v =	20	40	80	160	320	640	1280	2560
(Shukoff)	Λ^{25° =	*84*	*93*	*100*	*106*	*112*	*120*	*131*	*149*
(*e*) $TlPr_3Br$	v =	128	256	512	1024	2048	4096		
	Λ^{25° =	70	76	80	89	106	136		
(*f*) $TlBu_3Cl$	=		80	89	106	122	144		
(*g*) $TlCl_3$	v =	2	4	8	16	32	64	128	
(Meyer)	Λ^{0° =	*105*	*122*	*145*	*176*	*223*	*307*	*437*	
	Λ^{25° =	*144*	*178*	*207*					
h) $TlBr_3$	v =	19·4	38·8	77·6	155·2	310	620	1240	2480
	Λ^{25° =	23	25	28	33	43	78	87	124
		(No change with time						......)	183 (1 hr.) 210 (3 hrs.)

(ii) *Molecular Conductivities of Thallium Bases in Water at 25°.*

(*a*) TlOH	v =	*2*	*4*	*8*	*16*	*32*	*64*	*128*	*256*
(Ostwald)	Λ^{25° =	*182*	*200*	*217*	*230*	*238*	*244*	*248*	*248*
(*b*) $TlMe_2OH$	v =	8·13	16·33	32·65	65·3	130·6	261·2	522·4	1045
(Hein)	Λ^{25° =	*107*	*127*	*143*(?)	*157*	*165*	*169·5*	*167·6*	*164·1*
(c) $TlEt_2OH$	v =	9	18	36	72	144	288	576	1152
(Hein)	Λ^{25} =	*100·1*	*116·3*	*131·2*	*144·8*	*153·1*	*154·6*	*153·8*	*149·8*
(*d*) $TlPh_2OH$	v =	8	16	32·1	64·2	128·3	256·6	513·3	1026·6
(Hein)	Λ^{25° =	*98·7*	*113·6*	*127·1*	*139·8*	*148·4*	*151·6*	*150·3*	*145·1*
(*e*) $TlPr_2OH$	v =			50	100	200	400	800	1600
	Λ^{25° =			120	131	139	143	144	140
(*f*) $TlBu_2(OH)$	v =				89	178	350	712	1424
	Λ^{25} =				126	127	141	138	131

(c) *Dialkyl Bases.*—The evidence that the dialkylthallonium halides are extensively hydrolysed in dilute solutions indicates

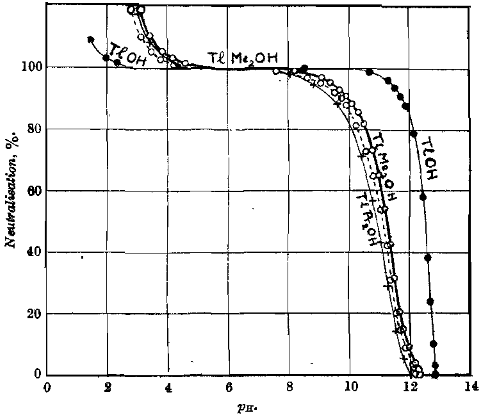
that these salts are derived from relatively weak bases, which a ionised only incompletely and reversibly in solution. This co clusion was established by observations of the molecular cond tivities of the free bases, which are set out in Table III (ii), a are plotted against the square root of the concentration in Fig. *Since data were already available for the dimethyl, diethyl,* a diphenyl bases (Hein and Meininger, *Z. anorg. Chem.*, 1925, **145**, 9 we have examined only the dipropyl and dibutyl compounds, wh *we prepared in the usual way* by use of silver oxide from *Goddard's specimens of the halides.* As a standard of compari we have taken Ostwald's data for thallous hydroxide (*J. pr. Che* 1886, **33**, 352; 1887, **35**, 112), since this base shows the typ behaviour of a strong electrolyte. Thus, the curve showing relation between Λ and $\sqrt{c}$ is linear from $N/2$ to $N/128$, and c begins to droop at a dilution of $N/256$, owing probably to increasing influence of carbon dioxide in the conductivity wa The data of Hein and Meininger, then, show that, whilst the r Λ/Λ_{∞} is about 85% for thallous hydroxide at $v = 8$, the corresp *ing percentages for aqueous solutions of the dimethyl, diethyl, diphenyl bases are* 41·8, 42·0, and 42·4 at $v = 8{\cdot}02$, 9·0, and respectively. These ratios can no longer be used as a direct mea of the ionisation of the base, but, since the conductivities of dialkyl bases at $v = 8$ are only about half as great as thos thallous hydroxide, the coefficient of ionisation of these b cannot be greater than about 50%. This conclusion is confi by the data for the dipropyl and dibutyl bases, where the con tivities are even lower in the linear portion of the curves, whil *drooping of the curves at dilutions beyond* $N/128$ corresponds c *with that of the curves plotted* from the data of Hein and Mein

Electrometric Titrations.

A preliminary titration of a $N/10$-solution of dimethylthallo hydroxide against N-hydrochloric acid with a hydrogen elec confirmed the conclusion that the hydroxide could not be c with the alkalis as a " strong " base; but it did not provide a worthy measure of the strength of the base. A direct comp was therefore made between $N/10$-thallous hydroxide and dimethylthallonium hydroxide with the help of a glass elec which had been *in constant use for some months, and ga* $E.M.F.$ of 54 millivolts per unit of p_H. The bases were titrate N-sulphuric acid, in order to avoid the precipitation of the spa soluble dimethylthallonium chloride, which had been obser the preliminary experiment; a saturated solution of pot sulphate was used as a junction liquid to the calomel electrode

resulting curves are shown in Fig. 6, together with a curve deduced from the readings of a hydrogen electrode immersed in the same solution. These curves show that, whilst thallous hydroxide behaves as an alkali, the dimethyl base is of a lower order of strength ($-\log K_b = 3$), and is presumably ionised only incompletely and reversibly. The accuracy of the data was confirmed by the fact that a titration with a glass electrode of the dipropyl base at a con-

FIG. 6.



Potentiometric titration of bases.
Full lines = glass electrode.
Broken line = hydrogen electrode.

centration of $N/14{\cdot}3$ gave a curve which followed that for the dimethyl base, with a steady deviation of about 0·2 unit on the side corresponding with the curves for weak bases.

Absorption Spectra.

All the dialkylthallonium halides that we have studied are colourless salts, but the absorption spectra of the dimethyl chloride and iodide were examined in order to ascertain if there was any characteristic absorption in the ultra-violet. The molecular extinction coefficients in water and in methyl alcohol are plotted in Fig. 3. The contrast between the two salts appeared at first to support the view,

which we had deduced from the conductivity data, that the dialkyl halides are ionised only reversibly in solution; but, when the solutions of the iodide were photographed against equivalent solutions of potassium iodide, the extinction coefficients were found to be practically identical with those of the chloride, and are therefore an additive function of the absorption of the two ions. The ratio Λ/Λ_∞ at $N/100$ is about 50% in methyl alcohol and may be estimated at 65% in water (where Λ_∞ cannot be determined directly, on account of hydrolysis): the proportion of undissociated salt in the $N/50$ solutions used for the measurements of absorption was probably at least one-half in methyl alcohol and one-third in water. The additive relation cannot therefore be explained away by the electrolytic dissociation of the salt in the dilute solutions used for the spectroscopic measurements, but must be admitted to hold good also for the undissociated molecules of the salt. On the other hand, in view of the regularity with which covalent iodides, including even methyl iodide itself, give rise to very strong absorption bands in the ultra-violet region, it seems unlikely that the selective absorption of thallium tri-iodide would disappear completely in dimethylthallonium iodide, if the iodine in the latter compound were linked to the halogen by a real bond. We can therefore only conclude that, in this case, the spectroscopic data are in closer accord with Fajans's theory of aggregates of deformable ions as a cause of incomplete electrolytic dissociation, than with the view that a low conductivity always implies the formation of covalent molecules.

General Conclusions.

The chemistry of thallium presents certain peculiarities which await an explanation in terms of the electronic theory of valency Thus, it is remarkable that *thallium*, although a third-group metal forms a series of very stable univalent thallous salts, whilst *gold* which might be expected (like silver) to be most stable in the forn of a univalent kation, gives rise generally to tervalent auric salts Again, the alkyl derivatives, instead of being of the types AuEt an $TlEt_3$, interleaving with $HgEt_2$ and $PbEt_4$, are of the types AuEtBr, $AuEt_2Br$ (Pope and Gibson, J., 1907, **91**, 2061) and $TlMe_2I$ (Meye and Bertheim, *loc. cit.*). These apparent anomalies, however, fin a simple interpretation in the following observations. (i) The ele ments Au, Hg, Tl, Pb have escaped from the domination of th *octet* rule, but are still subject to the *duplet* rule (compare *Tran Faraday Soc.*, 1928, **24**, 31); any even-numbered aggregate electrons, from 78 up to 86, can therefore form a stable system. in the case of the acids (*ibid.*, p. 1), this dominance by the duplet ru

is very favourable to reversible ionisation. (ii) As has long been recognised, metallic mercury, with its low boiling point and monatomic vapour, possesses some of the characteristics of an inert gas, although, as Sidgwick has pointed out ("Electronic Theory of Valency," p. 179), it contains two electrons more than are required to complete the outer shell of 18 O-electrons; it therefore provides, with niton, an electronic configuration of maximum stability, which the intermediate elements tend to take up in their various compounds. (iii) Mercury and thallium are related to one another in the same way as carbon and nitrogen, so that a molecule in one series becomes an ion in the other, as in the well-established case of CH_4 and $\overset{+}{N}H_4$. The significance of these considerations can be seen from the following table.

Number of electrons.	78	80	82	84	86
(*a*) *Gold.*	Au^{+}	$AuCl$	$AuCl_3$	$AuCl_4^{-}$	
(*b*) Mercury.	Hg^{++}	Hg Hg_2^{++}	$HgPh_2$ $HgCl_2$ Hg_2Cl_2	$HgCl_3^{-}$	HgI_4^{--}
(*c*) Thallium.	Tl^{+++}	Tl^{+}	$TlPh_2^{+}$ $TlMe_2^{+}$ $TlBr_2^{+}$	$TlBr_3$ $TlMe_2I$ $TlMe_2OH$	$TlCl_3^{--}$ $TlBr_4^{-}$
(*d*) Lead.	Pb^{++++}	Pb^{++}	$PbEt_2^{++}$	$PbEt_3^{+}$	$PbEt_4$

(i) *80 Electrons. The univalent thallous ion, with 80 electrons* round the nucleus, as in the atom of elementary mercury, retains its charge just like the ion of an alkali metal, *e.g.*, in concentrated solutions of thallous salts and of thallous hydroxide, and even in crystals of thallous chloride and bromide, which are built on the same face-centred cubic lattice as cæsium chloride. The hydrolysis of dilute solutions of thallous fluoride (Kohlrausch and Steinwehr, *Sitz. Preuss. Akad. Wiss. Berlin*, 1902, **26**, 581) and of thallous oxalate (Abegg and Spencer, *Z. anorg. Chem.*, 1905, **46**, 406) has been cited as evidence of the weakness of the base, but, since the conductivity of thallous hydroxide is equal to that of the alkalis, and no hydrolysis has been detected in thallous chloride, nitrate, etc., we may suppose that it is the weakness of the acid rather than of the base which is responsible for the hydrolysis. There is therefore no evidence that the 80 electrons of the ion are converted into the system of 82 electrons which would be present in the covalent molecule, TlOH, of a reversibly-ionised base.

(ii) 81 *Electrons.* A more serious reflexion on the stability of the thallous ion is found in Drucker's suggestion (*Z. Elektrochem.*, 1922, **28**, 463) that univalent thallium forms diatomic kations, like mercury, but by a reversible process, $2Tl^{+} \rightleftharpoons Tl_2^{++}$. In the case

of mercury, the formation of a diatomic kation makes it possible to formulate the mercurous ion with 80 electrons round each nucleus, just as in the monatomic vapour, and thus to maintain the duplet rule; in the case of thallium, however, this process would increase the number of electrons round each nucleus from 80 to 81, and thus provide an exception to the duplet rule. This hypothesis was introduced as a device to interpret the freezing points, transpor numbers, and conductivities of thallous nitrate over the rang $0{\cdot}04$—$0{\cdot}14N$ (as well as certain data for thallous sulphate) on th basis of Ostwald's dilution formula, and without using the theory o strong electrolytes. It leads to a ratio $Tl_2^{++}/Tl^+ = 1/7$ at $N/1$(but is not supported by any independent evidence, and can be rule out on the ground that, whilst the presence of pairs of mercur atoms can be inferred from the X-ray analysis of crystalline calome the same type of evidence shows equally clearly that the atoms (thallium in the thallous halides are present exclusively as sing atoms or univalent ions.

(iii) 82 *and* 84 *Electrons.* The univalent dialkyl ions of the ty $TlMe_2^+$ correspond to the covalent molecules, $HgPh_2$ and HgC of the mercury series, with 82 electrons round the nucleus. I marked contrast to the univalent thallous salts, the dialkyl halid do not obey the formulæ for strong electrolytes; the bases fro which they are derived are also considerably weaker than thallo hydroxide, and can no longer be classed with the alkalis as exampl of "complete ionisation." There can therefore be little doubt th the dialkyl halides, and the bases from which they are derived, well as the corresponding trihalides and their bases, are capable yielding non-conducting molecules, such as $TlMe_2I$, $TlMe_2OH$, a $TlBr_3$, which are of the same order of stability as their univale ions. The spectroscopic evidence, however, indicates that the nc conducting forms of these salts may be ionic doublets, rather th covalent molecules. The existence of systems in which the thalli nucleus is surrounded by 84 electrons in molecules such as TlMe and $TlBr_3$ is therefore less well-established than in the case of mercury, where it is unlikely that the three halogens in the $HgBr_3^-$ are related unequally to the metal. The doubt which t arises as to the real existence of the 84-electron system, with onl electrons less than the next inert gas, may furnish a clue to reason why it has not been found possible to prepare the trial derivatives of thallium, since these could not be expected to e

in a form corresponding with the ionised molecules of $\overset{+}{Tl}Me_2\overset{-}{I}$, could therefore only be produced if the 84-electron system v stable.

(iv) 86 *Electrons.* The complex mercury salts of the type $NH_4^+[HgBr_3]^-$ sometimes assume the more stable configuration of niton by combining with a molecule of water; but they do this even more readily by taking up a second molecule of the alkali halide as in K_2HgI_4, etc. In the case of thallium, a similar tendency is seen in the conversion of the deliquescent crystals of thallic chloride and bromide into beautifully crystalline and sparingly soluble salts of the type $Tl^+[TlBr_4]^-$, where the atom of thallium inside the bracket has at last assumed the niton configuration which we find also in $PbCl_4$ and in $PbEt_4$. Another example of the niton configuration is found in the double thallous salt 2AgCl,TlCl, which crystallises from a molten mixture of the silver and thallous chlorides, and to which the structure $Ag_2^{++}[TlCl_3]^{--}$ may be assigned. In complex anions of the type $Tl_3[TlCl_6]$, however, the outer 8-electron shell of the inert gas is replaced by a 12-electron shell, just as in the 6-co-ordination compounds of cobalt and platinum.

(v) 78 *Electrons.* The formation of the 78-electron group in Au^+, Hg^{++}, Tl^{+++}, and Pb^{++++} involves the removal of two electrons from the stable mercury configuration. This becomes progressively more difficult as the charge on the ion increases, so that we cannot be sure whether the relatively high conductivity of aqueous solutions of thallic chloride is due to the ability of the salt to behave as a quaternary electrolyte or merely to hydrolysis; on the other hand, the low conductivity of the salt in non-aqueous solutions shows that, under less favourable conditions, it behaves only as a binary electrolyte, $TlCl_3 \rightleftharpoons \overset{+}{Tl}Cl_2 + \overset{-}{Cl}$ (compare $TlMe_2I \rightleftharpoons \overset{+}{Te}Me_2 + \overset{-}{I}$). The existence of thallic ions in infinitesimal quantities can, however, be inferred from potentiometric measurements.

Summary and Conclusions.

(*a*) Thallium tri-iodide has been examined in order to determine whether it should be regarded as thallic iodide, or as a thallous polyiodide. Solutions in methyl alcohol and acetonitrile form addition compounds with pyridine and chloropyridines, and complex ions with potassium iodide, and exhibit the general reactions of a thallic salt, but the reactions of thallous ions could not be detected with certainty.

(*b*) The absorption spectrum of the tri-iodide in methyl alcohol shows two maxima, but these are separated by 1400 Å.U., whereas those of potassium tri-iodide are separated only by 650 Å.U. The spectrum is therefore not that of a tri-iodide ion, nor can the compound be a simple aggregate of tervalent thallium and univalent iodide ions, since these ions are colourless and do not give rise to

any absorption bands. The iodide is therefore regarded as a tervalent compound, in which a part at least of the halogen is linked directly to the metal.

(c) The molecular conductivities of the thallium trihalides in methyl alcohol and in acetonitrile are less than those of potassium iodide; the salts therefore behave only as binary electrolytes, in which some of the halogen is linked to the metal, *even in the most* dilute alcoholic solutions.

(d) Dimethylthallonium iodide is hydrolysed in dilute aqueous solutions and is derived from a base which is much weaker than thallous hydroxide. The molecular conductivity of thallic bromide is less than that of a binary electrolyte, except in dilute aqueous solutions where it is hydrolysed progressively.

(e) The properties of thallium are discussed on the basis of the hypothesis that mercury and thallium are related to one another in the same way as carbon and nitrogen.

The authors desire to express their gratitude to Mr. Heycock for his interest in the work, to Dr. Dootson for presenting them with specimens of chloro-derivatives of pyridine, and to Dr. Goddard for specimens of the dialkylthallonium halides.

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CCXXVI.—*The Influence of Constitution on the Stability of Racemates.*

By ALEXANDER FINDLAY and ALAN NEWTON CAMPBELL.

ALTHOUGH a large number of determinations of the freezing-point curves of optically active substances have been carried out, little is known with regard to the range of stability of racemates and the influence of composition or constitution on the transition point. For the purpose of obtaining information on this matter, the solubility relations of a series of related optically active esters have been determined at temperatures between 0° and 40°. The freezing-point curves of the esters were also determined where these were not already known.

For the purpose of our investigation the following substances were employed: tartaric acid, the methyl esters of tartaric acid and of diacetyl-, dipropionyl-, and dibenzoyl-tartaric acids, and the ethyl esters of diacetyl- and dibenzoyl-tartaric acids.

The solvent, where not otherwise stated, was an aqueous alcohol containing 93·8% of alcohol by weight; $d_{15^\circ}^{15^\circ} = 0{\cdot}8128$. The

solubilities were determined with the active form, with the racemic form, and with a mixture of the active and racemic forms as solid phases. In the case of solutions containing both the active and the inactive forms, the composition was determined polarimetrically, the variation of the specific rotation with concentration and in presence of the inactive form having been previously determined.

(1) *Tartaric Acid.—Freezing-point curve.* The freezing points of mixtures of *d*- and *l*-tartaric acids were determined by Centnerszwer (*Z. physikal. Chem.*, 1899, **29**, 715), and from the resulting curve the conclusion was drawn that *d*- and *l*-tartaric acids form a continuous series of solid solutions. We are unable to confirm this. Owing to the difficulty with which crystallisation takes place, we have determined, not the freezing-point, but the melting-point curve of mixtures, and on plotting the latter a eutectic is found at 161·6° and 94·3% of the *d*-acid. The experimental values are as follows * :

d-Acid, %	100	95	94·3	93	87·6	50
M. p.	168·5°	162·5°	161°	170°	195°	205°

The facts that the melting point of the racemic is much higher than that of the active acid, and that the melting-point curve of the racemic acid extends over such a long range of composition, indicate that the freezing point is far removed from the transition point. The very flat summit of the freezing-point curve indicates that the racemic molecules are largely dissociated in the molten state.

Solubility. The solubilities of the *d*-acid, of anhydrous racemic acid,† and of mixtures of these in 100 g. of alcohol are :

Solid phase.	Solubility (g./100 g. alcohol).			
	0°	15°	25°	40°
d	25·17	30·65	43·04	61·70
r	2·006*	3·153*	5·01*	6·299*
d + *r*	24·92 *d* / 1·09 *l*	40·26 *d* / 0·2 *l*	51·06 *d* / 1·04 *l*	94·04 *d* / 1·58 *l*

* Total *d* + *l*.

For the sake of comparison, the solubility in water at 25° was also determined; it is expressed as g. of anhydrous tartaric acid to 100 g. of water, but the hydrated racemic acid was present as solid phase.

$$d\ 147{\cdot}7\,;\ r\ 21{\cdot}5\ (d+l)\,;\ d+r\begin{cases}103{\cdot}8\ d\\ 11{\cdot}8\ l\end{cases}$$

* Since the melting-point or freezing-point curve is symmetrical on either side of the line representing the composition of the racemic form, only half the complete curve is given here.

† Perkin (J., 1887, **51**, 367) has shown that racemic acid crystallises from alcohol uncombined with solvent.

When the solubilities in alcohol are plotted with rectangular co-ordinates (*Roozeboom, Z. physikal. Chem.*, 1899, **28**, 494), a curve is obtained of the form which shows that the racemate exists as stable solid phase in contact with the solution. Owing to the fact that the solubility curve for the racemate occupies such a large portion of the diagram, even at 0°, it is clear that the transition point, if one exists, must lie far below zero.

(2) *Methyl Tartrate.*—The active ester melts at 48°, and the racemic at 85°. The melting-point curve for mixtures of the methyl *d*- and *l*-tartrates was determined by Adriani (*Z. physikal. Chem.*, 1900, **33**, 467). The curve for the racemic compound occupies a large part of the diagram, the composition at the eutectic point (42°) being 97% of *d*-ester. The solubility curves also show that the methyl racemate is far removed from its transition point even at 0°. The following are the solubilities in 93·8% alcohol:

Solid phase.	Solubility (g./100 g. solvent).			
	0°	15°	25°	40°
d	62·05	199·3	324·5	580
r	16·30	20·88	29·2	55·82
d + *r*	52·05 *d*	88·44 *d*	101·4 *d*	254·5 *d*
	10·25 *l*	10·44 *l*	12·65 *l*	20·5 *l*

(3) *Methyl Diacetyltartrate.*—This ester was prepared by the acetylation of the methyl tartrate. The active ester prepared from methyl *d*-tartrate is lævorotatory.

The fusion or melting-point curve was determined by Adriani (*loc. cit.*). We have determined the following values of the freezing points of mixtures of the active and racemic esters:

d-Ester, %	100	93·05	83·7	79·1	66·9
F. p.	102·5°	98·0°	94·0°	90·1°	86·0°
d-Ester, %	63·1	59·5	54	52·3	50·0
F. p.	85·8°	82·1°	79·8°	79·5°	79·8°

The curve constructed from these data is shown in Fig. 1. It agrees in form with the melting-point curve obtained by Adriani. The temperature of the eutectic point is 79° and the eutectic mixture contains 53·6% of the *d*-ester.

The molecular depression of the freezing point of the racemic ester was found to be 4955, tartaric acid being used as solute. With the help of this value, the degree of dissociation of the racemate was calculated from the slope of the freezing-point curve (Kremann, *Z. Elektrochem.*, 1906, **12**, 259), and found to be about 10%. In the liquid methyl diacetylracemate, therefore, at its freezing point, about 90% of the racemic molecules must exist undissociated.

The following values for the solubility in 93·8% alcohol were obtained:

Solid phase.	Solubility (g./100 g. of solvent).					
	0°	15°	20°	25°	32°	40°
d	0·0378	2·14	—	7·025	—	16·65
r	3·02	5·20	—	11·59	25·0	37·4
d + *r*	1·51 *l*	2·60 *l*	4·11 *l*	2·72 *l*	—	16·9 *l*
	1·51 *d*	2·60 *d*	4·11 *d*	8·87 *d*		26·6 *d*

On plotting the solubility values in rectangular co-ordinates, the curves shown in Fig. 2 are obtained. From the figure, it is seen that up to about 20°, the solubility curve consists of only two branches. Below 20°, therefore, the solid racemic ester is not stable. At 25°

Fig. 1.

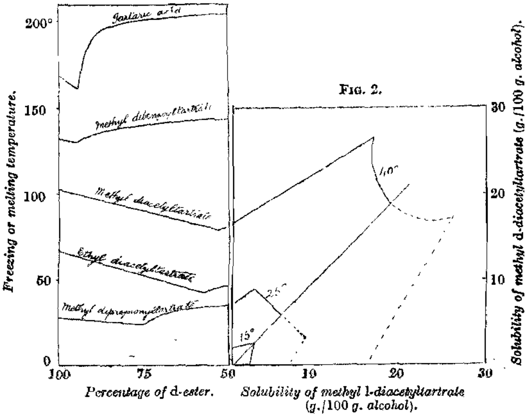

Fig. 2.

and above, the solubility curve consists of three portions, indicating the stable existence of the racemic ester in contact with the solution. The transition point must therefore lie in the neighbourhood of 20°.

The transformation of the racemic into the active esters takes place with great slowness at temperatures below the transition point. It was found, for example, that when the active and the racemic ester were brought in contact with alcohol at a temperature below 20°, a period of a week or more elapsed before equilibrium was attained.

In order to determine the transition point, curves were drawn representing the solubility of the solid phases *d* + *r*, *r*, and *d* + *l*

respectively. The point of intersection of these three curves, which should take place at the transition point, is 23·4°. Great accuracy cannot, however, be claimed for this determination.

The angle of intersection of the solubility curves for $d + l$ mixtures and for the racemic form is small, indicating a small heat of transformation. Accurate determinations of the transition point by means of a dilatometer were not possible owing to the slow rate of transformation of the racemic ester. The value found was between 21·2° and 25·9°.

Determinations of the solubility in carbon tetrachloride were also carried out, and the following values obtained :

Solid phase.	Solubility (g./100 g. of carbon tetrachloride).			
	0·2°	15·0°	25·0°	37·2°
d	1·6	3·73	5·4	9·16
r	2·18	3·66	6·3	16·6
d + *r*	1·03 *d* 1·03 *l*	1·72 *d* 1·72 *l*	4·1 *d* 2·8 *l*	10·32 *d* 4·93 *l*

These data also indicate a transition point between 20° and 25°.

Since the transition point may be taken as 23°, it should be possible to resolve the racemic ester by crystallisation at temperatures below 23°, just as Pasteur obtained a resolution of sodium ammonium racemate. Our attempts to secure such a resolution, however, have had only a very partial success. On one occasion, on allowing a solution to crystallise at the ordinary temperature, one relatively large crystal was picked out which melted at 103°, the m. p. of the active ester. On other occasions, however, bunches of ingrowing crystals were deposited, and it was not possible to distinguish crystals of opposite activity by their outward form. The same difficulty, indeed, was met with in the case of the resolution by crystallisation of rubidium racemate (Traube, *Neues Jahrb. Min.*, *Beil.-Bd.*, 1895—96, **10**, 795).

Very feebly active crystals were obtained by crystallisation from solutions in carbon tetrachloride at −17°.

The conclusion that the racemic ester is unstable below about 23° is in harmony with the results obtained by Anschütz and Pulfrich (*Annalen*, 1888, **247**, 121), who found from cryoscopic measurements in acetic acid solution that the racemate is completely dissociated (compare Bruni and Padoa, *Atti R. Accad. Lincei*, 1902, [v], **11**, i, 212).

(4) *Ethyl Diacetyltartrate.*—The active and racemic esters were prepared by acetylation of the corresponding ethyl tartrates. The *racemic ester* boils at 172°/20 mm., and melts at 48·3° (Found : C, 50·0 ; H, 6·0. $C_{12}H_{18}O_8$ requires C, 49·7 ; H, 6·2%). The ester

prepared from ethyl *d*-tartrate is dextrorotatory. The freezing-point curve (Fig. 1) can be constructed from the following data:

d-Ester, %	100	97·17	93·85	88·5	81·2
F. p.	66·6°	65·2°	63·0°	60·3°	56·1°
d-Ester, %	61·6	57·0	53·7	51	50
F. p.	45·8°	42·8°	44·6°	45·9°	46·0°

At the eutectic point, 42·0°, the mixture contains 55·7% of the *d*-ester.

The solubilities in alcohol are as follows:

Solid phase.	Solubility (g./100 g. solvent).			
	0·9°	15·0°	24·2°	38·9°
d	6·03	13·8	38·1	178
r	16·15	53·2	146	—
d + *r*	11·5 *d* 2·5 *l*	40·5 *d* 23·5 *l*	101·75 *d* 49·25 *l*	

The transition point must obviously lie considerably below 0°.

(5) *Methyl Dipropionyltartrate.*—These esters were prepared by Freundler's method (*Ann. Chim. Phys.*, 1894, **3**, 450). The *racemate* melts at 34·2° (Found: C, 49·5; H, 6·1. $C_{12}H_{18}O_8$ requires C, 49·7; H, 6·2%). The ester prepared from methyl *d*-tartrate is lævorotatory.

Owing to the readiness with which supercooling occurs, it was found advisable to determine, not the freezing-point, but the melting-point curve. The following values were obtained:

d-Ester, %	100	95·5	79·3	71	61·5	54·5	50·0
M. p.	27·5°	27·0°	25·7°	28·5°	33·3°	34·0°	34·2°

At the eutectic point, 24°, the mixture contains 75% of *d*-ester.

Owing to the very great solubility of these esters in all common solvents, we have refrained, for the present, from determinations of the solubility curve. With 40% alcohol and with light petroleum, the active ester forms two liquid layers at the ordinary temperature.

(6) *Methyl Dibenzoyltartrate.*—The active ester prepared from methyl *d*-tartrate is lævorotatory, and melts at 132°. The *racemic ester* melts at 144·5° (Found: C, 61·4; H, 4·5. $C_{20}H_{18}O_8$ requires C, 62·2; H, 4·7%); owing to its slight solubility, it is somewhat difficult to purify.

The following freezing points were obtained:

d-Ester, %	100	99·42	98·29	96·17	94·5	92·45
F. p.	132·0°	131·8°	131·3°	130·7°	130·4°	132·5°
d-Ester, %	86·6	66·4	58·2	52·2	50·7	50·0
F. p.	136·2°	141·5°	142·5°	142·8°	143·2°	143·3°

The eutectic point lies at 130·4° and 94·5% of *d*-ester.

The molecular freezing-point depression of the racemic ester, witl tartaric acid as solute, was found to be 7055. From this it wa calculated that the molten racemate is dissociated to the extent o about 20%.

The following solubilities in alcohol were determined :

Solid phase.	Solubility (g./100 g.). 15·6°	25°
d	0·165	0·323
r	0·07	0·236
d + *r*	0·266 *d*	0·455 *d*
	0·047 *l*	0·210 *l*

The solubility data show that at the above temperatures th racemic ester is stable in contact with the solution and that it i far removed from its transition point.

(7) *Ethyl Dibenzoyltartrate.*—Since the active ester has a ver high solubility and crystallises with very great difficulty (Franklan and Wharton, J., 1896, **69**, 1585), further investigation of it was no undertaken. The *ethyl* r-*dibenzoyltartrate*, however, was purifie by repeated recrystallisation (Found : C, 63·4; H, 5·3. $C_{22}H_{22}O$ requires C, 63·8; H, 5·3%). Since it melts at 105°, whereas th active ester melts at 62·5°, it is probable, on analogy with othe esters which we have investigated, that the racemic ester woul be far removed from its transition point even at the ordinar temperature.

When one studies the melting points and melting-point or freezing point diagrams of the compounds which we have investigated, it i found that the difference between the melting points of an activ and a racemic acid (tartaric acid) is but little, if at all, affected b esterification. The difference between the m. p.'s of *d*- and *r*-tartari acids is about 37°, and the same difference (85°—48°) is found in th case of the *d*- and *r*-methyl esters. The range of composition throug which the racemic form is stable is also but little altered. Intr duction of an acyl group into the ester, however, lowers the m. p of the racemic as compared with the active ester, and shortens th range of existence of the freezing-point curve for the racemic form Specially effective in this respect is the acetyl group; its effective ness in diminishing the range of stability of the racemic form i shown also by the realisation of a transition point at about 20° Whether similar relationships are also to be found in the case o other optically active esters is now being investigated.

Summary.

1. The freezing-point and solubility curves of active and racemi forms of tartaric acid, of its methyl ester, of the methyl ester o

diacetyl-, dipropionyl-, and dibenzoyl-tartaric acids, and of the ethyl ester of diacetyl- and dibenzoyl-tartaric acids, have been studied.

2. The introduction of an acyl group into the methyl or ethyl ester of tartaric acid lowers the melting point of the racemic form relatively to that of the active form, and reduces the range of stability of the racemic form. In this respect, the acetyl group is much more effective than the propionyl or the benzoyl group.

3. The transition point of methyl diacetylracemate lies at about 23°.

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CCXXVII.—*Cryoscopic Irregularities with Phenols.*

By GEORGE MAXWELL RICHARDSON and PHILIP WILFRED ROBERTSON.

IN spite of extensive investigation, the forces causing deviation from Raoult's law are still but poorly understood, especially where solvents and solutes possess such ill-defined electrochemical character as is found with organic compounds. Early attempts to account for such cryoscopic irregularities were based variously on theories of solute ionisation or association, of solvate formation, and of separation of solid solutions, yet their inadequacy has now necessitated the introduction of thermodynamic concepts. The consequent emphasis on intermolecular forces suggests the possibility of correlating cryoscopic irregularities with those physical properties (*e.g.*, molecular volume, viscosity, vapour or osmotic pressure) which are governed by such forces. In this paper, which continues previous investigations of typical organic liquids in phenol solution (Robertson, *J.*, 1903, **83**, 1425; 1904, **85**, 1617; 1905, **87**, 1574; 1906, **89**, 567), cryoscopic measurements have been accompanied in typical cases by simultaneous determination of the alteration in molecular volume of the liquid solutes upon addition to the solvent.

Cryoscopic Deviations.

Calculation of Results.—The molecular depression constant $K = \Delta Mb/100a$ for Raoult's equation was calculated after successive additions of solute in amount sufficient to cause a depression increasing from 0·5° to 5·0°. These depression "constants" were then plotted against the depressions, and the values of K at depressions of 1° (K_1) and of 3·5° ($K_{3\cdot5}$) were read off from the curves. A simple qualitative expression for the deviation was then obtained

by expressing the difference between these constants ($K_{3\cdot5} - K_1$) as a percentage of the depression constant at 1° (K_1). The "percentage deviations," $100(K_{3\cdot5} - K_1)/K_1$, so obtained are numerically equal to approximately one-third of Robertson's "rate" of association.

Table I contains the values obtained for K_1, $K_{3\cdot5}$, and the percentage deviation for alcohols, phenols, anilines, anilides, and amides, also *pyridine and quinoline*, in phenol solution.

TABLE I.

Alcohols.	K_1	$K_{3\cdot5}$	% Dev.
Methyl	67·4	67·4	0
Ethyl	68·1	69·2	+ 1·6
Propyl	65·2	68·2	+ 4·6
*iso*Propyl	66·5	68·6	+ 3·2
Allyl	67·0	67·4	+ 0·6
*iso*Butyl	68·1	68·9	+ 1·2
n-Octyl	68·2	68·7	+ 0·7
Cetyl	62·6	55·2	−12·0
Benzyl	68·1	68·2	+ 0·1
Anilines.			
Aniline	69·1	70·5	+ 2·0
o-Toluidine	68·0	71·2	+ 4·7
m-Toluidine	68·3	71·7	+ 5·0
p-Toluidine	68·6	71·9	+ 4·8
p-Bromoaniline	68·5	69·4	+ 1·3
s-Tribromoaniline	68·0	63·9*	− 7·5
Substituted Anilides.			
Aceto-*p*-toluidide	71·7	75·9	+ 5·9
Chloroaceto-*p*-toluidide	70·6	74·0	+ 4·8
Propiono-*p*-toluidide	70·0	73·7	+ 5·3
Aceto-*p*-bromoanilide	71·1	72·5	+ 2·0
Phenylaceto-*p*-bromoanilide	69·3	70·9	+ 2·3
Glutaro-*p*-bromoanilide	77·4		
Dinono-*p*-phenylenediamide	75·4		
Dihepto-*p*-phenylenediamide	75·8		

Phenols.	K_1	$K_{3\cdot5}$	% Dev.
m-Cresol	43·4	41·6	− 4·1
Resorcinol	55·0	53·0	− 3·6
o-Cresol	53·4	52·0	− 2·6
Pyrocatechol	54·7	53·4	− 2·4
o-Chlorophenol	57·1	55·7	− 2·5
p-Cresol	65·5	64·4	− 1·7
Quinol	60·3	58·1	− 3·6
p-Chlorophenol	66·3	65·2	− 1·7
s-Tribromophenol	68·8	66·9	− 2·9
Anilides.			
Acetanilide	69·5	72·9	+ 4·9
Phenylacetanilide	70·9	74·5	+ 5·1
Chloroacetanilide	69·6	70·8	+ 2·0
Propionanilide	68·5	72·0	+ 5·2
n-Butyranilide	70·5	73·4	+ 4·1
*iso*Butyranilide	70·5	72·8	+ 3·3
n-Octoanilide	71·5	73·6	+ 2·9
Palmitanilide	68·8	66·2	− 3·8
Succinanilide	74·1	83·5	+12·7
Azelanilide	70·6		
Sebacanilide	75·1		
Amides.			
Acetamide	69·5	74·6	+ 7·3
Phenylacetamide	70·3	74·2	+ 5·5
Chloroacetamide	68·3	70·8	+ 3·7
Pyridine	68·8	74·7	+ 8·6
Quinoline	65·1	69·0	+ 6·0

* Owing to the limited solubility of tribromoaniline this figure is for a depression of 3°. For the percentage deviation a correction has been made.

A general perusal of these deviations reveals two main tendencies: (1) As an homologous series is ascended, deviations of K increase at *first in a positive direction*, but *at the fourth carbon atom a reversal occurs until in the long-chain carbon compounds deviations finally* become negative (compare alcohols and anilides); (2) substitution by a phenyl group produces no regular change of deviation, but substitution by a halogen atom tends to produce negative deviation (compare aniline with *p*-bromo- and *s*-tribromo-aniline; anilides with *p*-bromoanilides; chloroacetanilide and chloroacetamide with the unsubstituted compounds).

These tendencies, noted already by Robertson in his investigations on acids and esters, would seem to be general in all homologous series, and to point to a differentiation of the effect on percentage deviation of the hydrocarbon chain and of the attached polar group. In the view of Hildebrand (*J. Amer. Chem. Soc.* 1916, **38**, 1452), osmotic phenomena are considered to be the

observable expression of intermolecular forces induced (*a*) by the internal pressure and (*b*) by the polarities of the interdiffused liquids. Since relative internal pressure among homologues presumably varies as the size of the molecule, whereas polarity is largely dependent on the attached group, this view may be regarded as receiving confirmation in these results.

Another feature of the table not so readily explained is observed with the cresols, where, although noticeable parallelism is shown by the depression curves, the molecular depression constants are markedly dissimilar whatever the concentration. Bruni's explanation involving the separation of solid solutions is not applicable here even if we accept his analytical technique (see Robertson, *loc. cit.*, 1906); for, first, van Bijlert (*Z. physikal. Chem.*, 1891, **8**, 352), using this technique, found no separation of solid solution whatever with *m*-cresol, whereas in its depression constant this is the most irregular phenol; secondly, crystallographic data reveal marked divergence in crystal structure among compounds found to exhibit very similar molecular depressions; and finally, while morphotropic considerations indicate that *p*-substitution, in affecting least the symmetry of the molecule, favours similarity of crystal structure between the simple and substituted compounds, in this investigation the greatest deviation is found with *o*- and *m*-substituted compounds. A theory of active molecules propounded by Brown and Bury (*J. Physical Chem.*, 1926, **30**, 694) provides no better explanation, since it involves regularity at infinite dilution and has no explanation for parallel depression curves.

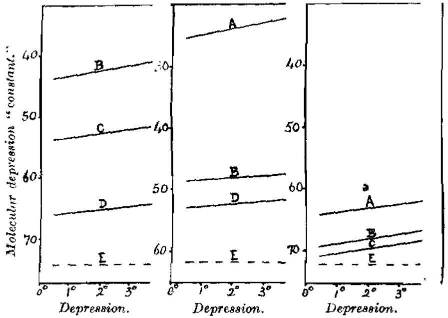
Further light was sought by investigating *o*- and *p*-cresol as solvents for simple phenols; the curves shown in Fig. 1 were obtained. The remarkable parallelism of curves would seem to indicate the formation of solid solutions, as would also the fact that phenol–*o*-cresol and phenol–*p*-cresol mixtures show abnormalities of like extent whichever component be in excess. However, the characteristically greater abnormality of *m*-cresol, as compared with *o*- or *p*-cresol, in each of the structurally different solvents is incompatible with this conclusion, and the previous criticisms have been in no wise invalidated.

The smaller abnormalities disappear almost completely if a mean depression constant (69) for the homologous series investigated is used for comparison in preference to the van 't Hoff theoretical constant ($K = 0{\cdot}02T^2/L = 74$). Hence the explanation of abnormality may be that in phenolic solutions the van 't Hoff equation requires considerable modification to include some theory of active molecules, though the theory of Brown and Bury cannot be accepted in its present form.

Variations of Molecular Volume.

Calculation of Results.—The alteration of molecular volume of the solute is expressed as the ratio (Molecular solution volume)/(Molecular volume), where the molecular volume is derived from the density of the pure liquid at 40°, and the molecular solution volume is calculated on the simple mixture law from the solution density at 40° of that solution which produces a depression of 4·5° in the freezing point of phenol. Thus the solutions are of approximately the same molecular concentration, but the assumption is made that the

FIG. 1.



A = *Phenol as solute.* C = o-*Cresol as solute.*
B = m-*Cresol as solute.* D = p-*Cresol as solute.*
E = $0{\cdot}02T^2/L$ (*calculated value for* K).

whole change of volume upon solution takes place in the molecul of the smaller component.

The molecular volume changes in the various binary liqu mixtures are tabulated in Tables II*a* and *b*, where *p* is the percer age composition required to produce a depression of 4·5°. Dire determinations of density at 40° were made except for the molecul volumes of the pure simple alcohols, which were obtained by ext polation of their known densities at other temperatures. Figu for a hydrocarbon, an ester, and an acid are also included, si each of these types shows a characteristic deviation curve.

It is noted from Table II (*a*) that the alcohols show a typically l ratio of M.S.V./M.V., whereas the phenols (omitting the not un pected exceptional values for halogen derivatives) show little volu

TABLE II.

(*a*) Phenol as solvent. K (experimental mean) = 69·0.

Solute.	p.	M.S.V.	M.V.	M.S.V./M.V.	$K_{4\cdot5}$.	Deviation, %
Methyl alcohol	2·2	40·0	41·6	$0{\cdot}96_1$	67·5	0
Ethyl alcohol	3·1	57·2	59·6	$0{\cdot}96_0$	69·5	+ 1·6
Propyl alcohol	4·0	73·1	76·3	$0{\cdot}95_8$	68·3	+ 4·6
*iso*Propyl alcohol	3·8	74·4	78·0	$0{\cdot}95_4$	69·2	+ 3·2
Allyl alcohol	3·8	69·1	71·1	$0{\cdot}97_2$	67·4	+ 0·6
*iso*Butyl alcohol.........	5·1	90·2	94·5	$0{\cdot}95_4$	69·3	+ 1·2
n-Octyl alcohol	7·5	157·0	159·8	$0{\cdot}98_2$	68·8	+ 0·7
Cetyl alcohol	21·0	282·9	294·0	$0{\cdot}96_2$	52·5	−12·0
Benzyl alcohol	7·2	104·5	104·9	$0{\cdot}99_7$	68·5	+ 0·1
m-Cresol	11·7	105·9	106·1	$0{\cdot}99_7$	40·7	− 4·1
o-Cresol	9·1	104·8	105·0	$0{\cdot}99_8$	50·6	− 2·6
o-Chlorophenol	10·6	104·8	103·6	$1{\cdot}01_2$	55·0	− 2·5
p-Cresol	7·9	106·0	106·1	$0{\cdot}99_8$	63·9	− 1·7
p-Chlorophenol	9·0	104·2	101·6	$1{\cdot}02_8$	64·8	− 1·7
Toluene	6·6	104·6	108·4	$0{\cdot}96_4$	61·3	− 5·4
Ethyl malonate	9·5	153·4	154·8	$0{\cdot}99_0$	80·0	+11·0
Acetic acid	4·4	58·3	58·3	$1{\cdot}00_0$	—	—

(*b*) *o-Cresol and p-cresol as solvents.*

	o-Cresol, K (mean) = 56·0.				*p*-Cresol, K (mean) = 70·0.			
Solute.	p.	M.S.V./M.V.	$K_{4\cdot5}$.	Dev., %.	p.	M.S.V./M.V.	$K_{4\cdot5}$.	Dev., %.
Toluene	8·3	$0{\cdot}97_5$	48·9	− 8·0	6·4	$0{\cdot}97_2$	62·3	−6·2
Ethyl malonate ...	11·4	$0{\cdot}99_4$	64·8	+10·0	9·0	$0{\cdot}98_8$	79·8	+5·3
*iso*Propyl alcohol	5·0	$0{\cdot}96_1$	53·6	+ 0·6	3·9	$0{\cdot}95_7$	68·5	+0·2
Acetic acid	4·3	$0{\cdot}97_5$	—	—	4·4	$0{\cdot}99_2$	—	—
p-Cresol	9·0	$0{\cdot}99_8$	51·1	− 2·1	—	—	—	—
o-Cresol	—	—	—	—	6·7	$0{\cdot}99_1$	67·9	−2·7
m-Cresol	9·6	$0{\cdot}99_9$	47·1	− 2·3	7·6	$0{\cdot}99_7$	65·8	−2·8
Phenol	*16·6*	$1{\cdot}00_5$	*20·9*	− 9·6	6·4	$1{\cdot}00_4$	60·6	−2·5

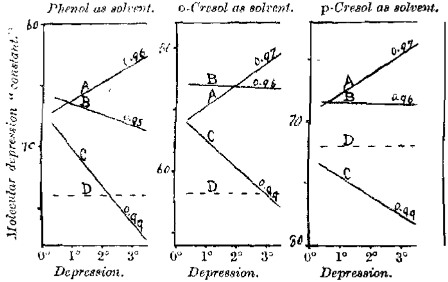
change. Benzyl alcohol, though alcoholic in cryoscopical behaviour, behaves in volume change as a benzene derivative. The absence of volume change in mixtures of phenols is confirmed in Table II (*b*), so that, whatever the nature of the molecular environment *producing such divergent magnitudes for K, it has no effect on* molecular volumes. It is therefore not surprising that the depression curves of these phenolic mixtures are found to be parallel.

TABLE III.

Solute.	Toluene.	*m*-Xylene.	*iso*Amyl acetate.	*o*-Cresol.	Phenol.	*p*-Cresol.
Toluene	—	$1{\cdot}00_6$	$1{\cdot}00_3$	$0{\cdot}97_5$	$0{\cdot}96_4$	$0{\cdot}97_2$
Ethyl malonate	$1{\cdot}02_6$	$1{\cdot}02_6$	$1{\cdot}02_3$	$0{\cdot}99_4$	$0{\cdot}99_6$	$0{\cdot}98_8$
o-Cresol	$1{\cdot}02_5$	$1{\cdot}01_8$	$0{\cdot}98_8$	—	$0{\cdot}99_8$	$0{\cdot}99_1$
m-Cresol	$1{\cdot}02_2$	$1{\cdot}01_2$	$0{\cdot}98_5$	$0{\cdot}99_9$	$0{\cdot}99_7$	$0{\cdot}99_7$
Phenol	$1{\cdot}03_0$	$1{\cdot}01_4$	$0{\cdot}98_2$	$1{\cdot}00_5$	—	$1{\cdot}00_4$
p-Cresol	$1{\cdot}01_5$	$1{\cdot}01_8$	$0{\cdot}98_5$	$0{\cdot}99_8$	$0{\cdot}99_8$	—
*iso*Propyl alcohol	$1{\cdot}04_3$	$1{\cdot}02_8$	$1{\cdot}02_4$	$0{\cdot}96_1$	$0{\cdot}95_4$	$0{\cdot}95_7$
Acetic acid	$1{\cdot}07_6$	$1{\cdot}03_6$	$0{\cdot}89_4$	$0{\cdot}97_5$	$1{\cdot}00_0$	$0{\cdot}99_2$
Mean (excluding acetic acid)	$1{\cdot}02_7$	$1{\cdot}01_5$	$0{\cdot}99_6$	$0{\cdot}99_0$	$0{\cdot}98_5$	$0{\cdot}98_5$

To strengthen any conclusions based on volume changes, molecular volume changes were determined with the unassociated toluene, *m*-xylene, and *iso*amyl acetate as solvents. These figures, together with those for the phenols, are in Table III, where both solutes and solvents are arranged in order of their " degree of association " in the liquid state. It would appear that unassociated solvents have the effect of increasing the molecular volume of solutes in solution. Yet generalisations based on concepts of molecular association require solutes in normal solvents to be associated, and to have, almost certainly, smaller molecular volumes, so that these figures enlarge the increasing mass of evidence which

FIG. 2.



A = *Toluene as solute.* C = *Ethyl malonate as solute.*
B = *isoPropyl alcohol as solute.* D = $0 \cdot 02T^2/L$ (*calculated value for K*).

discredits the widespread use of " association " concepts to explai irregular behaviour in intermolecular phenomena (see Brown an Bury, *loc. cit.*, p. 702). It is significant that *iso*propyl alcohol an acetic acid, which would commonly be regarded as the mo " associated " of the solutes, show this contrary result in molecul volume change to the greatest extent.

General Discussion.

Results for solutes of the three types, alcohol, ester, and hydr carbon, in the three phenolic solvents are compared in Fig. (Type phenols have already been discussed, and comparison wi type acids is invalidated by large polar effects.) The figures plac on each curve represent the ratio M.S.V./M.V., and it seems obvic that each typical deviation is accompanied by an equally typi

alteration of the molecular volume. Hence it becomes significant to enquire whether the intermolecular forces causing this volume change are also capable of governing the cryoscopic deviations.

Referring first to volume changes and to Table III, we find that the anomaly there remarked vanishes if we explain the results in terms of internal pressures, since a solute of internal pressure similar to that of its solvent will be dissolved without volume change, whereas a solute of smaller internal pressure would be compressed on solution, or *vice versa*. By forming a general estimate of internal pressures in this way, we find that their descending order for our compounds is : acetic acid, *iso*propyl alcohol, the phenols and ethyl malonate, the hydrocarbons and amyl acetate—a good agreement with generalisations from Mortimer's internal-pressure data (*J. Amer. Chem. Soc.*, 1923, **45**, 633). The marked irregularity of phenols and acetic acid when dissolved in amyl acetate is a good illustration of specific disturbing influences which may arise out of polar groups.

Referring now particularly to the solutes of Fig. 2, we find that in toluene and xylene solutions, ethyl malonate and *iso*propyl alcohol are expanded and toluene is normal, whereas in phenolic solutions, the ester is normal and toluene and *iso*propyl alcohol are compressed. This anomalous behaviour with alcohol–phenol mixtures is satisfactorily attributed to the tendency towards chemical combination of the molecules resulting in a closer binding and a smaller molecular volume.

Correlation between the deviation of the cryoscopic constant and these demonstrated internal-pressure differences is now sought. Hildebrand (*J. Amer. Chem. Soc.*, 1916, **38**, 1473; 1919, **41**, 1078) finds that in mixed liquids difference of internal pressure produces positive deviation from Raoult's law, since such a mixture results in smaller molecular attractions and increased vapour pressure, thereby reducing the " lowering of vapour pressure " and the amount of change in boiling point or freezing point. This diminution results in that increase of molecular weight (or decrease of K) so commonly stated to be due to " association." Inequality of polarity produces a like effect, but with two highly polar liquids deviation is found to be negative.

Toluene and phenol show differences in both internal pressure and polarities (as estimated qualitatively from dielectric constants); they reveal a marked decrease of K with concentration. Ethyl malonate and phenol possess similar internal pressures and are both highly polar; K increases markedly with concentration. *iso*-Propyl alcohol and phenol possess different internal pressures and polarities, but show a tendency to unite; the expected decrease

in K is balanced by the increase due to a tendency to solvate formation. The cresols have internal pressures similar to that of phenol, but lower polarities; for each solute, the cresols show deviations of a slightly less positive character than phenol.

Thus a very interesting relation between deviations from cryoscopic normality and changes in molecular volume seems to have been established, and to be correlated with a difference of internal pressures and polarity of the intermixed liquids; but until further data have accumulated it is impossible to formulate more trustworthy conclusions. Since throughout the investigation great care was taken to eliminate as far as possible any error due to the hygroscopic nature of the solvents or other experimental sources of irregularity, it is considered that the deviations observed were conditioned by the forces governing interaction of solvent and solute.

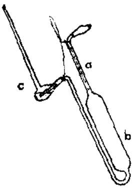
Finally, we append a table of densities ($d^{40°}_{40°}$) of various liquids:

Acetic acid ...	1·0291	Phenol	1·0586	*o*-Chlorophenol	1·2416
*iso*Amyl acetate	0·8524	*o*-Cresol	1·0290	*p*-Chlorophenol	1·2651
Ethyl malonate	1·0349	*m*-Cresol	1·0184	Toluene	0·8498
Allyl alcohol ...	0·8166	*p*-Cresol	1·0186	*m*-Xylene	0·8487
Benzyl alcohol	1·0303				

EXPERIMENTAL.

The Beckmann apparatus with magnetic stirring device wa employed in the cryoscopic work. Determinations were made wit considerable care, and by adopting speci precautions—notably a cooling bath insulate with cotton-wool and maintained at 35° ov a steam boiler—highly comparable results we obtained.

FIG. 3.



Density determinations of pure liquids amounts of about 3 c.c. were made in a special constructed pyknometer of volume known . 40° (Fig. 3). With the trap *c* turned dow wards, the liquid was aspirated into t weighed pyknometer *b* until it reached the sca on the arm *a*, which was next closed with rubber cap. Then the pyknometer, inserted in its containi vessel in the position shown in the figure, was immersed in t thermostat at 40°; when equilibrium was reached, the vessel w tilted to displace the liquid in the trap from the mouth of t pyknometer, the volume was read to 1/10,000 c.c. from the sca and cooling was allowed in this position. Then the trap w removed and the second weighing made.

Solution densities were determined in a special long-neck

specific-gravity bottle, graduated at 40° to read to 0·001 c.c. over the range 13·5—14·0 c.c. The final solution from the Beckmann apparatus was transferred directly to the bottle by means of a long-pointed pipette of the same capacity, the volume was read off after equilibrium was attained in the thermostat, and weighings were made. It is believed that through the use of these methods, the experimental error in the final ratio M.S.V./M.V. is no greater than 0·5%.

The best materials obtainable commercially were used. Liquids were further purified by drying and repeated fractionation until the b. p. of the accepted sample varied by no more than ± 0·1°. Solids were successively recrystallised, generally from aqueous alcohol, until the correct m. p.'s were obtained. The amido- and anilido-compounds were prepared from pure constituents by treating the base directly with the acid chloride of the appropriate acid (prepared by use of thionyl chloride). In certain instances this method was not applicable, and the methods indicated in the literature were adopted. The phenol, *o*-cresol, and *p*-cresol used as solvents were twice fractionated and twice recrystallised with the rejection of one-third during each operation, and gave final freezing points in good agreement with the literature. Suitable methods for successive deliveries of about 15 g. of solvent to the Beckmann tube without contact with the atmosphere were adopted.

Summary.

(1) The van 't Hoff equation ($K = 0{\cdot}02T^2/L$) does not hold for the solutes investigated, even at low concentrations.

(2) The observed deviations seem to depend on internal pressure and polarity in accordance with the theory of Hildebrand.

(3) Derived phenols have been found to show in their binary mixtures marked divergences not traceable to these causes. The theories of solid solutions and of activity (as formulated by Brown and Bury) have been shown to be unsatisfactory as explanations, but some theory of activity seems to be required.

(4) A general relation is shown between changes in molecular volume upon solution and cryoscopic behaviour, and this relation is in agreement with deductions drawn from internal-pressure data.

(5) Densities of various phenols and other compounds have been determined at 40°.

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CCXXVIII.—*The Alkaline Hydrolysis of Esters in Aqueous Alcoholic Solution. Part II. The Interaction of Phenoxides and Aliphatic Esters.*

By ERIC STEPHEN GYNGELL.

IT was shown in Part I (J., 1926, 2484) that the reaction between ethyl acetate and potassium phenoxide, in alcoholic solution, did not follow the usual bimolecular law, as required by the equation $C_6H_5{\cdot}OK + CH_3{\cdot}CO_2Et \longrightarrow C_6H_5{\cdot}OEt + CH_3{\cdot}CO_2K$, but was due to small amounts of potassium hydroxide produced by hydrolysis of the phenoxide by water present in the alcoholic solution. Alcoholysis of the phenoxide did not appear to be a cause of reaction.

A mathematical expression was deduced which gave satisfactory constants for the ester hydrolysis; the value of this constant, however, was the product of the velocity coefficient and an equilibrium constant, but it was not possible to determine these two factors separately with any degree of certainty.

Smith (J., 1927, 170) extended this work to the interaction of potassium *m*-tolyloxide and ethyl acetate in aqueous alcoholic solution, and obtained similar results. Numerous esters of the aliphatic series have now been studied, and in all cases, except for esters of oxalic acid, the reaction has been found to proceed as a result of hydrolysis of the phenoxide.

EXPERIMENTAL.

The following experiment is typical of the whole series. Time is expressed in minutes and concentrations in milliequivs. per litre.

Potassium phenoxide, *N*/4; ethyl propionate *N*/4; H_2O, 2%; Temp., 70°.

Time.	Titre.	x.	$a - x$.	$b - x$.	$Kk \times 10^4$.
0	20·0	0·0	500·0	1111	—
70	13·8	155·0	345·0	956	1·04
136	12·4	190·0	310·0	921	0·98
180	11·5	212·5	287·5	898	1·05
240	11·0	225·0	275·0	886	0·95
300	10·2	245·0	255·0	866	1·01
355	9·8	255·0	245·0	856	0·99
				Mean	1·00

In the following table are shown the values of the constants for various percentages of water for the esters examined, the concentration of the ester and phenoxide being *N*/4 in every case and the temperature 70°.

Water, %.	0·2	1·0	2·0	3·5	5·0	10·0	20·0
Ester.				$Kk \times 10^4$.			
$CH_3 \cdot CO_2Me$	1·26	1·79	1·25	—	—	0·67	0·57
$CH_3 \cdot CO_2Pr^{\alpha}$	2·23	2·06	1·85	1·71	1·52	1·35	—
$CH_3 \cdot CO_2Bu^{\alpha}$	—	—	1·56	—	1·45	0·98	—
$CH_3 \cdot CO_2Bu^{\beta}$	—	2·35	2·83	1·58	1·50	1·39	—
$CH_3 \cdot CO_2C_5H_{11}(iso)$	—	2·57	2·76	2·37	2·13	1·85	—
$C_2H_5 \cdot CO_2Me$	—	—	0·87	0·83	0·81	0·73	—
$C_2H_5 \cdot CO_2Et$	—	—	1·00	0·87	0·73	0·68	—
$C_2H_5 \cdot CO_2Pr^{\alpha}$	—	2·57	1·04	0·84	—	0·77	—
n-$C_3H_7 \cdot CO_2Me$	—	—	0·62	0·62	0·52	0·47	0·56
n-$C_3H_7 \cdot CO_2Et$	—	—	0·61	0·64	0·55	0·43	0·30
n-$C_3H_7 \cdot CO_2Pr^{\alpha}$	—	—	0·66	0·58	0·42	0·34	0·28
n-$C_3H_7 \cdot CO_2Bu^{\beta}$	—	0·51	0·47	0·44	0·31	0·23	0·24
n-$C_3H_7 \cdot CO_2C_5H_{11}(iso)$	—	—	—	—	—	1·17*	0·90

* $Kk \times 10^4 = 1·12$ at 15%.

Relative Activities of the Esters.—The values of Kk for the different esters do not appear to be strictly in order of the atomic weights. There is, however, a distinct decrease in the values of the constants from acetate to butyrate.

In conclusion, I should like to thank Dr. J. C. Crocker for his continued interest in the work.

CHELSEA POLYTECHNIC, S.W. [*Received, April 16th, 1928.*]

CCXXIX.—*Pseudo-ternary Systems containing Sulphur. Part III. The System Sulphur–Sulphur Monochloride.*

By DALZIEL LLEWELLYN HAMMICK and MICHAEL ZVEGINTZOV.

IT was noticed by Aronstein and Meihuizen (*Proc. K. Akad. Wetensch. Amsterdam*, 1898, **1**, 1) that a saturated solution of sulphur in sulphur monochloride, S_2Cl_2, after being heated to 170° and chilled, not only failed to deposit sulphur at its saturation temperature but was even capable of dissolving a further amount. This phenomenon was more fully investigated by Aten (*Z. physikal. Chem.*, 1913, **81**, 257). He pointed out that the behaviour of the sulphur solutions could be explained either by the formation of a new modification of sulphur as a result of the rise in temperature, or by the formation of a subchloride as a result of interaction between the dissolved sulphur and the solvent. Both effects could, of course, operate simultaneously. He heated saturated solutions of non-equilibrium sulphur (S_{λ}) to various temperatures between 50° and 170° and, after chilling them to 25°, 0°, and − 60°, determined the very considerable amounts of S_{λ} that the solutions would now dissolve before they became once more saturated. As a result of a somewhat elaborate

phase-rule analysis of the data obtained, he excluded the possibility of subchloride formation. Further, having found that insoluble or amorphous sulphur is insoluble in cold sulphur monochloride, and assuming that such sulphur is identical with S_μ (the form of sulphur present in equilibrium with S_λ in liquefied sulphur), he concluded that the increase in the amount of sulphur that the solntions would hold after heating could only be explained on the supposition that a new liquid form, S_π, was present. Aten subsequently estimated the amounts of S_π present in liquid equilibrium sulphur at various temperatures (*Z. physikal. Chem.*, 1913, **86**, 10) and found a maximum of 6·7% at 160°. This amount is quite insufficient to account for the large increases in the solvent power of sulphur–sulphur chloride mixtures found when such mixtures are heated and subsequently chilled. For instance, a solution of sulphur in sulphur chloride saturated at 20° contains 17% of S_λ; this solution, after being heated at 100° for a few hours, chilled, and again saturated at 20°, will contain 31% of dissolved S_λ. On Aten's view, this exaltation of the solvent power must be due to the solvent's effect on the internal equilibrium of the dissolved sulphur, considerable amounts of S_π being formed.

The validity of Aten's contention that subchlorides are not formed in sulphur–sulphur monochloride mixtures becomes doubtful in the light of the work of Ruff and Golla (*Z. anorg. Chem.*, 1924, **138**, 33) and of Bruni and Amadori (*Atti R. Accad. Lincei*, 1919, **28**, 217), who obtained indirect evidence for the existence of subchloride molecules. We have therefore sought for direct phase-rule evidence on the question from a detailed study of solid–liquid equilibria in the system, and have determined (i) the solubility curve of sulphur in sulphur monochloride under conditions such that the solutions might be expected to contain only S_λ, and (ii) the temperatures at which the solutions used in (i) were in equilibrium with solid after having been heated to various temperatures until internal equilibrium had been reached and then chilled.

EXPERIMENTAL.

The sulphur used was twice recrystallised from carbon disulphide or toluene and dried at 90°. The sulphur monochloride was distilled in an all-glass apparatus from excess of sulphur, to ensure absence of dichloride, and dried over calcium chloride; it distilled constantly at 138°.

Temperatures of equilibrium between solid phases and solutions were determined by the synthetic method used in previous work on sulphur systems (J., 1926, 1995; 1927, 493). The glass tubes were about 2 cm. in diameter and contained about 3 c.c. of solution. The

true solubilities of sulphur in sulphur monochloride (S_λ only in solution) were determined by warming the bulbs in a mechanically stirred paraffin-bath and finding in the usual way the temperatures at which the last small crystal was in equilibrium with the solution. Each bulb was then heated until internal equilibrium had been established at 100°, 148°, 178°, and 230—235° in thermostatic oil-baths. Equilibrium (as indicated by unchanged solid–liquid equilibrium temperatures) was established in 4—5 hours at 100°, 1·5 hours at 148°, and less than an hour at 178° and 230°. After the bulbs had been chilled by plunging them into ice and water (the 230—235° bulbs were chilled for 5 seconds at 100° and then put into ice), crystallisation was induced by cooling, in many cases seeding being necessary as well. A few of the solutions heated to 148°, and many of those heated to 178° and above, deposited monoclinic sulphur on cooling; this could be made to pass into rhombic by warming gently until almost all the crystals had disappeared and then recooling. The data obtained are given below. Solubilities are recorded as g. per 100 g. of solution.

TABLE I.

Solubility of Sulphur in Sulphur Chloride.

Temp.	−9°	2°	4°	10°	21°	28·7°	35·7°	36·8°
S, %	7·34	10·63	11·81	13·52	17·28	22·50	25·79	28·12
Temp.	41°	45·6°	47·6°	54·2°	56°	56·2°	60·2°	61·8°
S, %	30·68	34·91	37·4	42·64	44·7	44·81	49·69	51·70
Temp.	70·2°	71·5°	77·4°	82·4°	83·6°	86·8°	90·5°	92·6°
S, %	60·73	62·18	67·5	73·45	75·4	78·16	82·45	83·4
Temp.	92·5°	97·9°	96·7°	100·8°	101·6°	101·4°	110·3°	
S, %	85·9 (mono)	87·97 (mono)	88·42	89·35 (mono)	90·53 (mono)	93·18	97·02 (mono)	

In Table II solid–liquid equilibrium temperatures are recorded for solutions that had been heated at the specified temperatures and subsequently chilled.

TABLE II.

(*a*) Solid–liquid equilibrium temperatures after preheating at 100°.

Temp.	−30°	−22°	−15·5°	−11°	−6°	−3·3°	2·8°	8·4°
S, %	11·81	14·24	15·75	17·28	20·32	21·91	24·86	26·86
Temp.	14·5°	19°	24°	28·2°	32°	39·4°	46·5°	46·4°
S, %	29·29	30·68	34·91	37·4	40·04	44·7	51·2	51·7
Temp.	56·8°	59·4°	62·2°	65·3°	70·6°	71·5°	74·8°	79·2°
S, %	60·73	62·18	65·0	67·5	70·45	73·45	75·4	78·16
Temp.	85·6°	90·8°	94·4°	94·9°	97·4°			
S, %	82·45	85·9	87·97	88·42	89·35			

(*b*) *Solid–liquid* equilibrium temperatures after preheating at 148°.

Temp.	−18·5°	−14°	−9·5°	−8°	−4·5°	−0·7°	1°	2·3°
S, %	20·32	22·0	24·86	25·79	26·86	29·29	31·1	32·29
Temp.	5·5°	17°	17·5°	22·8°	27·8°	34°	36·2°	36·5°
S, %	22·15	37·4	37·96	42·64	44·7	50·29	51·2	51·7
Temp.	45° (mono)	53° (rhom)	57°	54·8° (mono)	68·5° (rhom)	70·4°	73·2°	80·5°
S, %	65		67·5	73·45		75·4	78·16	82·45
Temp.	80·8° (mono)	85·4° (rhom)	88·4°	79·6° (mono)	90·6°	109°		
S, %	85·9		87·97	88·42	89·35	97·02		

(*c*) Solid–liquid equilibrium temperatures after *preheating at* 178°.

Temp.	2·75°	5·0°	10·75°	12·0°	18·5°	23·5°	25·4°	28·0°
S, %	33·15	34·64	37·96	40·96	43·96	46·97	49·78	51·46
Temp.	32·2°	38·0°	41·0°	42·75°	51·5°	62·8°	70·0°	83·8°
S, %	52·8	57·39	61·31	64·76	68·55	73·45	78·16	85·9
Temp.	102·5°							
S, %	93·11							

(*d*) Solid–liquid *equilibrium temperatures* after preheating at 230—235°.

Temp.	36·6°	44·5°	53·5°	43·0° (mono)	58·6° (rhom)	54·5° (mono)	63·6° (rhom)	73·4°
S, %	55·3	61·31	68·55	70·43		73·06		79·13

The above results are plotted in the diagram ; some points hav been omitted on the sulphur side in order to avoid confusing th curves.

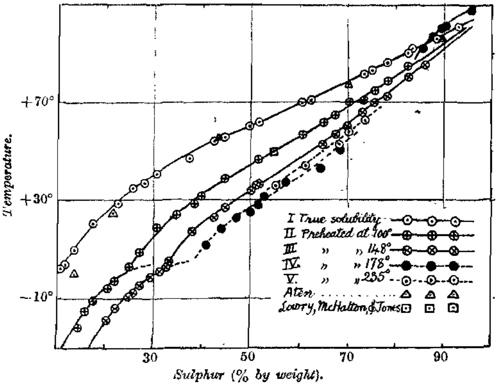
Discussion of Results.

It is necessary that the significance of the curves in the diagrar should be made quite clear. Curve I is taken to be the true solubilit curve for sulphur in sulphur monochloride, complications due t compound formation or shift of internal equilibrium having bee avoided by rapid working. The curve is in good agreement wit that of Aten (*loc. cit.*), whose points are indicated on it. Curve I is related to I as follows : At any temperature t° a point on Curve gives the amount of sulphur that must be added to saturate sulph monochloride without complications. When such a solution heated at 100° and then chilled, the temperature at which it is nc just saturated with sulphur (or other substance capable of givi a crystalline solid phase) is given by a point on Curve II vertical below the first point on Curve I. Curves III, IV, and V are similar related to Curve I.

It will be seen that Curves II and III show definite breaks in t neighbourhood of 0°. The lower portions in each case appear to

making for a maximum at a composition of about 34 parts of sulphur added to 66 parts of sulphur monochloride. This composition corresponds to a chloride S_4Cl_2. The solid phases that separate from solutions below 0° do not differ markedly in appearance from rhombic sulphur. That sulphur and sulphur monochloride are not the only substances present in the bulbs was shown, however, by opening them and removing the sulphur monochloride by means of a mercury-vapour pump and an activated-charcoal trap cooled in liquid air. A viscous, yellow oil was obtained, together with crystals of rhombic sulphur. On treatment with water, the oil gave hydro-

FIG. 1.



chloric acid with separation of sulphur, thus showing the presence of a chloride of sulphur. This could not be sulphur monochloride, which by itself is entirely volatilised and absorbed under the experimental conditions.

Confirmatory evidence that the portions of the Curves II and III correspond to a solid phase other than rhombic or monoclinic sulphur was obtained as follows. A bulb containing 30 parts of sulphur to 70 parts of monochloride was sealed and maintained at 148° for 2 hours. It was then chilled in cold water and placed in liquid air, a transparent glass being obtained. The bulb was opened and the mixture seeded with crystals of rhombic and monoclinic sulphur. No crystallisation occurred on warming and cooling

several times. A portion of the liquid contents of the bulb was now placed in a Dewar flask and stirred with a few drops of liquid air. After the latter had evaporated, the glassy mass softened and finally crystallised. A small portion of this crystalline mass was rapidly transferred to the bulb, which had been kept in liquid air. The contents of the bulb now crystallised on warming, a precipitate of small prisms melting at about 0° being obtained. Cooling of the bulb after these crystals had melted did not lead to separation of solid phase unless the liquid was seeded as before; the small crystals of rhombic and monoclinic sulphur originally added to induce crystallisation persisted, however, throughout. The same results were obtained on repetition several times with each of two separate bulbs.

It would thus appear to be established that at least one subchloride of sulphur is formed in heated solutions of sulphur in sulphur monochloride, and it is no longer necessary to suppose with Aten that unusually large amounts of forms of sulphur other than S_λ are formed in such solutions.

It is suggested that the formula of the new subchloride is S_4Cl_2 although there is no information available as to its molecular weight The simplest formula S_2Cl may be excluded on valency grounds S_4Cl_2 may reasonably be regarded as $\begin{matrix} S\leftarrow\!\!-S-Cl \\ \vert \\ S\leftarrow\!\!-S-Cl \end{matrix}$, in support c which its low volatility may be noted (compare Sidgwick, "Th Electronic Theory of Valency," p. 123).

Lowry, McHatton, and Jones (J., 1927, 746) have examined th whole system sulphur–chlorine. Unfortunately their results fo the portion of the system with which we have been concerned a given as a diagram without numerical data. We have calculate one solubility from a point on their graph and find that it lies o our curve for solutions that have been preheated at 100° (s diagram), as would be expected from the fact that their solutio were heated at 96° for a time before equilibrium temperatures we determined (*loc. cit.*, p. 753). Aten's solubilities (*Z. physik Chem.*, 1913, **81**, 274) are shown in the diagram, where it will seen that his points lie satisfactorily on our curve at the high temperatures. It may be noted that the statement of Low McHatton, and Jones that, after being heated to 170°, sulph dissolves permanently in sulphur monochloride (*loc. cit.*, p. 753) incorrect in the light of the data given in Table II (*c* and *d*). Ev after preheating at 230—235°, it was possible to determine eq ibrium temperatures down to 36·6°. The new chloride, S_4Cl_2, co not, however, be obtained as a solid phase from solutions prehea at 178° or 235°.

The data from the experiments with mixtures preheated at 178° nd 235° show that the enhanced solubility effect falls off as the reheating temperature rises, and that it is actually reversed at the ighest temperature. The following table gives the solubility of hombic sulphur at 50° in solutions that have been preheated at $T°$:

$T°$	—	100°	148°	178°	235°
S, %	39·5	54·5	62	68	66

In conclusion, it may be mentioned that solutions containing 25—40% of sulphur developed a distinct cloudiness when supercooled to − 75° after preheating at 148°. The opacity disappeared at about − 60° to − 50° on raising the temperature and appeared o be due to the separation of minute liquid droplets. It is thus ossible that a metastable two-phase (liquid–liquid) region had been ntered. The high viscosity of the solutions prevented adequate gitation of the liquid, so the clearing temperatures could not be ccurately observed.

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CCXXX.—*Effects induced by the Phenyl Group. Part I. The Addition of Polar Reagents to Styrene and the Behaviour of the Halogenated Ethylbenzenes.*

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ONE of the most striking exceptions to the Markownikoff rule was lescribed by Posner in his work on the addition of phenyl mercaptan o double bonds (*Ber.*, 1905, **38**, 646). He allowed various unsymnetrical unsaturated compounds to remain in contact with phenyl nercaptan and oxidised the sulphides produced to sulphones. These e compared with the sulphones obtained by the action of sodium enzenesulphinate on the bromide which was formed by the addition f hydrogen bromide to the respective unsaturated hydrocarbons. In each case the products from the two methods were different. He assumed each to be a pure substance and deduced that phenyl nercaptan added in the opposite sense to hydrogen bromide; *e.g.*,

$$CHPh{:}CH_2 \xrightarrow{HBr} CHPhBr{\cdot}CH_3 \xrightarrow{Ph{\cdot}SO_2Na} \underset{(I.)}{CHPh(CH_3){\cdot}SO_2Ph}$$

$$CHPh{:}CH_2 \xrightarrow{Ph{\cdot}SH} \underset{(II.)}{CH_2Ph{\cdot}CH_2{\cdot}SPh} \xrightarrow{KMnO_4} \underset{(III.)}{CH_2Ph{\cdot}CH_2{\cdot}SO_2Ph}$$

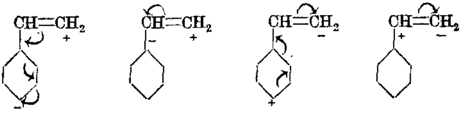
'. *Amer. Chem. Soc.*, 1916, **38**, 762; Allan, Oxford, Robinson, and mith, J., 1926, 406). The constants of a suitable group of acids nake it clear that, unlike saturated aliphatic or alicyclic groups, ohenyl has a stronger attraction than hydrogen for electrons negative general effect):

	$K . 10^{-5}$.		$K . 10^{-5}$.
Acetic	1·82	Benzoic	6·5
Propionic	1·31	Phenylacetic (?)	5·3
*yclo*Hexanecarboxylic	1·32	Phenylpropionic	2·3

he general effect on the constant of benzoic acid will be greatly educed by the conjugation CO·OH (IV), but may be omewhat increased by the steric effect of the phenyl group. The teric effect is, however, comparable in benzoic and *cyclo*hexane-arboxylic acids and both the steric and the conjugative effect are robably negligible in β-phenylpropionic acid, although here the eneral effect is also reduced by the length of the chain.

The chief result of this general effect on the side chain, apart from he conjugative effects which it may start, would be to make the -electrons more available than those on the α-atom, but it is super-mposed on any conjugative electronic displacements, in the manner liscussed by Lapworth and Robinson (*Mem. Manchester Phil. Soc.*, 928, **72**, 43) in their consideration of the *o* : *p* ratio in aromatic substitution.

Four types of conjugative electronic displacement affecting the eactions of the side chain are possible:



(A) (B) (C) (D)

None of tho known addition reactions (with the possible exception of hat with phenyl mercaptan, which will be discussed later) requires phase (B) (the direction of polarisation which would be initiated by the general effect due to the phenyl group); which would be relatively inactive to kationoid reagents, as the anionoid activity of the α-carbon would be reduced by the holding in of the electrons on that atom by the attraction of the phenyl group (general effect) and also by the steric effect of the phenyl group. One would also anticipate that in this phase and in (D) the α-atom would reduce its charge by conjugation with the nucleus, although the work of Farmer

and Thorpe on conjugated systems, of Scarborough, of Turner an of Kenyon and their collaborators on substituted diphenyl con pounds, suggests that the transmission of such polarisations is n necessarily very complete.

The polarisation in (D) is directly opposed to the general effe and if it is initiated by an increase of covalency between the nucle and the α-carbon atoms it approximates to phase (C). These are t phases which have the anionoid ω-carbon atom indicated by t reactions of the side chain, and something approximating to (must be considered the normal active phase of styrene.

This polarisation will not, however, explain the *o*-*p*-substitut in styrene and its derivatives, and the general effect of the vi group will tend to inhibit *o*-*p*-substitution, as this group has a grea attraction than hydrogen for electrons. This is clearly shown the dissociation constants :

	$K \cdot 10^{-5}$.		K . 1
Acetic acid	1·82	Vinylacetic acid	3·[illegible]
Butyric acid	1·47	Crotonic acid	2·[illegible]

(N.B. The general effect in crotonic acid is reduced by c jugation as in benzoic acid; compare above.)

Both the tendency to conjugate in the direction of (C) and and the attraction of the side chain for electrons will be incre in such derivatives of styrene as ω-nitrostyrene and cinnamic a and yet even in these cases *o*-*p*-substitution predominates. It only be assumed that in styrene and all these derivatives the some tendency to polarise in the manner (A) and this will hav activating effect on the o-p-positions, whereas the opposite pol ation (C) and the general effect will reduce the activity of al positions. Hence the polarisation of type (A) will facil ordinary substitution in the nucleus and those of type (C) w more inert in the nucleus and substitution will be facilitated in the ω-position. This is in keeping with the fact that styre nitrated in this position first.

It is anticipated that the detailed application of these theor considerations will be made clearer by experiments which a progress with derivatives of styrene containing substituents bo the side chain and in the nucleus.

Another type of evidence on the effects induced by the pl group was obtained by the action of boiling aqueous-alco caustic potash on the halogenated ethylbenzenes. Under conditions α-bromoethylbenzene gave quantitatively phenylme carbinol; β-bromoethylbenzene gave only styrene; and st dibromide gave pure α-bromostyrene. The last fact was prov hydrolysing the product with formic acid, isolating the a

phenone produced in 92% yield, and showing that ω-bromostyrene, which is inert towards formic acid, was absent from the residue. This is contrary to much previous work summarised by Nef (*Annalen*, 1899, **308**, 273) as follows :

"It is obvious that alcoholic potassium acetate, water at 190°, and alcoholic potash with styrene dibromide all give a mixture of α- and ω-bromostyrene, since the product has not a constant boiling point and gives phenylpropiolic acid on treatment with sodium and carbon dioxide. This can only be derived from ω-bromostyrene."

It was found, in the present investigation, that the boiling point rose rapidly from that of α-bromostyrene to that of unchanged styrene dibromide. The residue of the latter would account for the production of phenylpropiolic acid.

Neither α- nor β-bromoethylbenzene was reduced by hydriodic acid at 150° after four hours.

Ward has shown (J., 1927, 445) that the displacement of halogen n α-chloroethylbenzene is independent of the concentration of odium hydroxide used and up to 50° gives phenylmethylcarbinol vith optical inversion, but at 100° styrene, phenylmethylcarbinol, and αα'-diphenyldiethyl ether are formed. These facts he explains on the basis of a slow unimolecular reaction formulated in the way uggested by Nef :

$$C_6H_5{\cdot}CHCl{\cdot}CH_3 \longrightarrow C_6H_5{\cdot}\underset{/\ \backslash}{C}{\cdot}CH_3 + HCl$$

step supposed to be followed by either (1) the addition of water, r (2) isomerisation to styrene, or (3) addition of phenylmethyl-arbinol. He comments on the mechanism previously discussed by Phillips (J., 1925, **127**, 2567) dependent on the production of

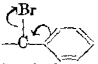
$\left.\begin{matrix}R_1\\R_2\\R_3\end{matrix}\right\rangle\overset{+}{C}$— *from a halogen compound by the removal of the halogen* on, but he retains the conception that, in such an ionisation, the ydrogen atom R_1 accompanies the halogen ion.

$$R_3\!:\!\underset{\underset{\displaystyle :\ddot{Cl}:}{\cdot\cdot}}{\overset{\overset{\displaystyle R_2}{\cdot\cdot}}{C}}\!:\!H \longrightarrow R_3\!:\!\underset{\cdot}{\overset{\overset{\displaystyle R_2}{\cdot\cdot}}{C}}\cdot + H\!:\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\!: \text{ not } R_3\!:\!\overset{\overset{\displaystyle R_2}{\cdot\cdot}}{C}\!:\!H + :\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\!:$$

The inversion in the formation of phenylmethylcarbinol could be ccounted for (compare Fischer, *Ber.*, 1907, **40**, 489; Lapworth and Mottram, *Mem. Manchester Phil. Soc.*, 1927, **71**, 63) if the removal f the halogen ion were dependent on one of the frequent approaches f the water or other solvent molecules, to the side of the α-carbon tom away from the halogen, occurring simultaneously with a rare

polarisation of the molecule sufficient to ionise the halogen under these conditions. This mechanism would also account for other observations which Ward discusses, namely, that solutions of potassium cyanide, ammonia, and potassium acetate in ethyl alcohol all give α-phenyldiethyl ether as the main product.

Many investigators (compare Conant and Kerner, *J. Amer. Chem. Soc.*, 1924, **46**, 232) have observed that phenyl and carbonyl groups have similar effects on the halogen atoms in systems of the form $R\cdot[CH_2]_n\cdot Cl$ (R=phenyl, carbethoxyl, etc.), phenyl being less powerful than any carbonyl group, and the results of the present investigation also show such similarities. It is to be noted from a theoretical point of view, however, that while the general effect of phenyl and carboxyl is in the same direction relative to hydrogen, the conjugative effects will depend on the nature of the side chain and the various factors may operate in different ways in different reactions of halogen atoms in the side chain. The α-halogen ir alkylbenzenes forms with the nucleus a type of allyloid system


(V) (Allan, Oxford, Robinson, and Smith, *loc. cit.*

in which the polarisation of the nucleus assists the tendency of th halogen atom to separate with a negative charge. This is in accor with the results of the investigations on the hydrolysis of substitute benzyl halides (*Ann. Reports*, 1927, **24**, 155), and also with tl capacity of the phenyl group for stabilising a positively charge α-carbon atom which is clearly shown in the positive triphenylmeth ion. The opposite polarisation (type A, p. 1793) and the gener effect may account for its less powerful effect in stabilising a negati charge in the sodium derivative of triphenylmethyl.

In the case of the β-halogenated ethylbenzenes the effect of tl phenyl group on the halogen atom, here separated from it by tv single bonds, appears to be slight, judged by the low reactivity potassium iodide in acetone (Conant and Kerner, *loc. cit.*). Assumi that the separation of the halogen ion is the first process in t production of styrene by the action of aqueous-alcoholic potassi hydroxide on ω-bromostyrene, this reaction will be dependent the ease with which the electrons of the α-carbon atom co-ordin with the ω-atom to form the double bond, as well as on the ease w which the halogen atom is removed. The conjugation with t nucleus (type C, p. 1793) will facilitate such co-ordination and t removal of the proton will follow. On the other hand, this react may be dependent on the tendency of the α-hydrogen to ion which will be increased by the opposite type of polarisation and general effect.

The repetition of Posner's experiments gave the products which he obtained, and the sulphone from the addition of phenyl mercaptan to styrene was identical with that obtained by the action of sodium benzenesulphinate on β-bromoethylbenzene. The sulphide obtained from the addition was also shown to contain less than 2% of the α-isomeride, by comparing the boiling point and refractive index with those of the two synthetic sulphides. It is therefore clear that phenyl mercaptan adds to styrene in the opposite sense to hydrogen bromide and other polar reagents, and the theoretical considerations which satisfactorily correlate those normal additions will not serve in this case if the reaction takes place between the polarised ethylene bond and the hydrogen and thiophenoxide ions.

In a search for other evidence in favour of a special mechanism for this reaction the course of the addition of phenyl mercaptan to styrene was followed by observations of the very large contraction in volume which takes place during the reaction and also by determinations of the depression of the freezing point of benzene caused by mixtures of phenyl mercaptan and styrene. The rate of addition is greatly dependent on the intensity of illumination, and the increase in rate produced by exposure to sunlight continues for some time after the reaction vessel is returned to diffused light; but the reaction was not stopped in the dark and the product was always phenyl β-phenylethyl sulphide. A small percentage of piperidine had such a powerful retarding action on the addition that no change in volume was observed in diffused daylight even after several days, although a contraction took place in sunlight. The action of light is well known to produce or enhance abnormal polarisations and depolarisations in a wide range of reactions, and experiments are in progress with a view to obtaining evidence in favour of one or other of the possible alternative mechanisms for the interaction of mercaptans with ethylenic hydrocarbons.

A remarkable isomerisation was observed in an attempt to prepare phenyl-β-phenylethylsulphone (III) by reducing phenacylphenylsulphone (VI) with zinc amalgam and hydrochloric acid: a liquid sulphide was obtained which on oxidation with hot chromic acid was converted into phenyl-α-phenylethylsulphone (I). A similar migration of groups takes place when ω-bromoacetophenone is heated with yellow ammonium sulphide (Willgerodt, *Ber.*, 1889, **22**, 534).

(VI.) $COPh{\cdot}CH_2{\cdot}SO_2Ph \longrightarrow$ (II.) or $CHPh(CH_3){\cdot}SPh$ (VII.) $\longrightarrow$ (I.)

Experimental.

Preparation of the Monohalogen Derivatives of Ethylbenzene.—Phenylmethylcarbinol (b. p. 100°/15 mm.; 3 : 5-dinitrobenzoate

m. p. 95°), made by the action of magnesium phenyl bromide on acetaldehyde, was converted by gaseous hydrogen bromide into α-bromoethylbenzene. This, by the action of silver acetate suspended in ether, readily yielded phenylmethylcarbinyl acetate which on hydrolysis gave the carbinol free from any detectable proportion of β-phenylethyl alcohol, as was shown by the properties of its 3 : 5-dinitrobenzoate and the entire absence of the fragrance associated with the isomeric compound.

The β-chloroethylbenzene used in some of the experiments described later was made by converting glycol chlorohydrin into it *p*-toluenesulphonate and leaving this in contact with a cold ethereal solution of magnesium phenyl bromide for 36 hours; about a equal weight of a liquid, which was probably ethylene chlorobromide was also produced (see Ferns and Lapworth, J., 1912, **101**, 273

β-Bromoethylbenzene was made by heating β-phenylethyl alcoh with constant-boiling hydrobromic acid for 24 hours; it had b. p 97°/12 mm., and was quite free from the pungent odour characterist of the α-bromo-compound.

Action of Aqueous-alcoholic Potassium Hydroxide on the Isomer Bromoethylbenzenes.—The two bromo-compounds, when heated on t water-bath under precisely similar conditions with aqueous-alcoho potassium hydroxide (about 0·4*N*), lost all the halogen (as det mined by the decrease in alkaline titres) within 30 minutes. In t product from the α-bromo-compound, no styrene whatever could detected. The product from the β-bromo-compound was almost pı styrene and absorbed bromine (1 mol.), yielding styrene dibromi

Addition Reactions of Styrene.—The styrene was made Howard's method from cinnamic acid (J., 1861, **13**, 136).

(A.) *Addition of hydrogen bromide.* A mixture of styrene an cold saturated solution of hydrogen bromide in glacial acetic acid kept over-night and then poured into water, and the oil obtained distilled (b. p. 95°/15 mm.). The product was nearly pure α-bro ethylbenzene, as it was converted, by means of silver acetate alkali successively, into phenylmethylcarbinol which gave characteristic 3 : 5-dinitrobenzoate (m. p. 95°) and had no detect odour of the isomeric β-phenylethyl alcohol (3 : 5-dinitrobenzo m. p. 108°).

(B.) *Addition of ammonium hydrogen sulphite.* An emulsio styrene (20 g.) with *N*/4-ammonium hydrogen sulphite (2 l.) kieselguhr (100 g.) was kept with frequent shaking for 10 d After filtration the liquid was boiled with excess of barium hydro until ammonia was expelled and worked up for soluble salts (pare J., 1925, **127**, 307); 8 g. (yield, about 16%) of colou *barium α-phenylethanesulphonate* were obtained in bundles of

eedles [Found: H_2O, 6·8; Ba (in anhydrous salt), 27·1. $C_8H_9SO_3)_2Ba,2H_2O$ requires H_2O, 6·6%. $(C_8H_9SO_3)_2Ba$ requires a, 27·0%]. No alkyl sulphite could be detected (compare *loc. cit.*). . portion of the salt was converted into the amide, which separated om alcohol in feathery crystals, m. p. 121°.

The sulphonic derivatives were identical with those obtained from e ammonium salt produced when α-bromoethylbenzene was heated ith aqueous ammonium sulphite for several hours (Found for the arium salt: H_2O, 6·9; Ba, in the anhydrous salt, 26·8%. Amide, athery crystals, m. p. 121°, mixed m. p. 121°).

As α-bromoethylbenzene shows little or no tendency to become onverted into styrene, the foregoing results indicate clearly that e sulphonic salt from styrene and hydrogen sulphite is the α-deriv- ive of ethylbenzene. The conclusion, however, was checked by reparing the β-sulphonic acid.

β-Bromoethylbenzene (8 g.) was boiled with aqueous ammonium ılphite, and the solution worked up as usual with barium hydroxide. *arium β-phenylethanesulphonate* (5 g.) was isolated in large, glisten- ıg plates [Found: H_2O, 3·4; Ba (iu anhydrous salt), 26·8. $C_8H_9SO_3)_2Ba,H_2O$ requires H_2O, 3·4%. $(C_8H_9SO_3)_2Ba$ requires a, 27·0%]. The sulphonamide melted at 124°.

(C.) *Addition of phenyl mercaptan.* The product obtained from yrene and phenyl mercaptan by Posner's method (*loc. cit.*) gave, n oxidation with cold dilute potassium permanganate solution and ccess of sulphuric acid, the pure β-sulphone, m. p. 56—57°, identical ith that prepared from β-bromoethylbenzene.

Phenyl α- and β-phenylethyl sulphides and the sulphide obtained ı fractionating the addition product were unattacked by hot or ld neutral potassium permanganate, even wheu it contained anganese dioxide in suspension. The addition of bromine or of ccess of dilute sulphuric acid caused rapid reduction of the per- anganate. If the oxidation was carried out hot, a mixture of ıenacylphenylsulphone (VI), m. p. 94—95°, and phenyl-β-phenyl- hylsulphone was obtained.

Phenyl-β-phenylethylsulphone (III) was prepared from β-bromo- ıylbenzene by boiling with an alcoholic solution of sodium nzenesulphinate for 12 hours and separated from carbon tetra- loride in feathery crystals, m. p. 56—57° (Found: S, 13·2. Calc. r $C_{14}H_{14}O_2S$: S, 13·0%). The sulphones could not he prepared om the chloroethylbenzenes, as the α-chloro-compound was con- rted into styrene and the β-isomeride was unchanged.

Pure phenyl α- and β-phenylethyl sulphides were prepared by ating sodium thiophenoxide (1·1 mols.) in alcoholic solution with or β-bromoethylbenzene (1·0 mol.), pouring the mixture into

water, and extracting the product with carbon tetrachloride. The sulphides were distilled, heated for ½ hour under reduced pressure at 100° in a stream of carbon dioxide, and redistilled. The α-compound had b. p. 163—164°/15 mm. and n_D 1·6042; the β-compound, b. p. 188—189°/15 mm. and n_D 1·6082.

The whole product of the reaction between styrene and phenyl mercaptan was washed with alkali, dried, and fractionated. The distinction between unchanged styrene, sulphide, and a small residue (probably metastyrene) was clearly marked. The middle fraction (yield, 90%), b. p. 187—190°/15 mm., heated in a stream of carbon dioxide under reduced pressure at 100° and refractionated, gave the following refractive indices: first 6 drops, 1·6079; 9 c.c., 1·6082; 2 drops, 1·6085; residue, 1·6088. Fractions 1 and 2 after refractionation gave: first 2 drops, 1·6073; 10 drops, 1·6081; thirteenth drop and the remainder, 1·6082. This indicates less than 2% of α-isomeride in the product.

Experiments on the velocity of the reaction and photocatalysis. During the reaction of styrene and phenyl mercaptan a 10% contraction takes place, and the course of the reaction was followed by cooling a mixture of styrene (11 c.c.) and phenyl mercaptan (10 c.c.) in a glass tube (0·2 to 0·5 cm. bore) in running water, marking the level of the meniscus, sealing the tube, and marking the level from time to time. As the velocity is influenced by light, the two reagents were distilled in only the light of a Bunsen flame (the mercaptan was distilled in hydrogen to prevent the formation of disulphide), and two tubes were prepared as described above, marked and sealed in a similar light, and left in a dark room. The part of each tube containing the liquid was kept inside rubber tubing down which water was running and the subsequent marks were made with a minimum of light in the dark room. The two reactions proceeded at the same rate. After 17½ hours one tube was taken into sunlight, the water-cooling being continued. The contraction was nearly doubled in the next 15 minutes and was practically complete after 1 hour. The other tube in the dark showed no signs of reaching the same limit after 3 weeks.

Time (hrs.)	0·1	1·5	2·5	14·0	17·5	17·75	18·0	18·25
Contraction (cm.) in tube I in dark	0·5	0·75	1·05	2·15	2·35	4·0*	4·4*	4·7*
Contraction (cm.) in tube II in dark	0·6	0·8	1·1	2·15	2·3			
Time (days)	1·5	2·5	3·5	4·5	6·5	8·5	22·5	25·5
Contraction (cm.) in tube I in light	4·9	4·9				4·9		
Contraction (cm.) in tube II in dark	2·6	2·95	3·25	3·4	3·6	3·75	3·8	3·8

* In sunlight.

The phenyl mercaptan remaining in the reaction carried out in the dark was extracted in alkali and the sulphide which was distilled out of the residue was shown to contain no detectable amount of the α-isomeride by determinations of the refractive index and boiling point.

A side tube was inserted about 70 cm. from the lower end of the reaction tube, the mixture was introduced until it overflowed from the side tube, and a similar experiment was carried out entirely in the dark. The speed was similar to that in the previous experiments before taking into sunlight.

Cryoscopic evidence on the course of the reaction [with CECIL ROBINS]. The freezing points were taken of solutions of phenyl mercaptan and of styrene in suitable amounts of benzene, and also the freezing points of the mixed solutions, with a view to determining whether any considerable amount of association took place quickly, followed by a photocatalytic depolarisation. No such association was observed and the rate of combination appeared to be in agreement with the velocity measured by contraction. In this case, however, it was clear that the reaction did not slow down again at once when the tube was returned to diffused light.

Action of Alcoholic Potassium Hydroxide on Styrene Dibromide.—Styrene dibromide (Glaser, *Annalen*, 1870, **154**, 164) (26·4 g.) was boiled in alcoholic solution with potassium hydroxide (1 mol.), the alcohol removed by distillation, and the oily product distilled in a vacuum. No fraction was obtained between α-bromostyrene and styrene dibromide.

The product was almost instantly attacked by boiling formic acid, the odour of acetophenone becoming perceptible. As β-bromostyrene was found to be very stable towards boiling formic acid, undergoing but slight hydrolysis after 20 minutes, this observation, which finds a parallel in the ready hydrolysis of α-chlorostyrene by hydrochloric acid, suggested a means of detecting β-bromostyrene when mixed with the α-isomeride.

0·774 G. of the lower-boiling portion of the product from styrene dibromide was boiled for about 5 minutes with formic acid, and sodium acetate and semicarbazide hydrochloride were then added; acetophenonesemicarbazone (0·653 g.; 92% of the theoretical yield) was deposited. It is evident that at least 92% of the oil consisted of α-bromostyrene. No trace of β-bromostyrene (easily detected by its powerful hyacinth-like odour) could be found in the liquor after the acetophenone had been removed. As a small quantity of unchanged styrene dibromide was present, having escaped the fractionation process, it is clear that removal of hydrogen

bromide from styrene dibromide takes place almost solely in one direction.

The authors gratefully acknowledge their indebtedness to Professor Lapworth for suggesting this investigation and for his advice and interest in it.

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CCXXXI.—*The Influence of the Intensity of Illumination on the Velocity of the Photochemical Union of Bromine and Hydrogen, and the Determination of the Mean Life of a Postulated Catalyst.*

By FRANK BRIERS and DAVID LEONARD CHAPMAN.

IN a previous communication (Briers, Chapman, and Walters, J., 1926, 562) experimental evidence was submitted in support of the contention of Berthoud and Bellenot (*Helv. Chim. Acta*, 1924, **7**, 307) that the rate of photochemical interaction of iodine and potassium oxalate in aqueous solution is proportional to the square root of the intensity of illumination. Formerly, it seemed to be not improbable that all photochemical changes would be found to be strictly proportional to the intensity of the light (*vide* Draper, *Phil. Mag.*, 1843, **23**, 401; M. C. C. Chapman, J., 1923, **123**, 3062; 1924, **125**, 1521; Kornfeld and Müller, *Z. physikal. Chem.*, 1925, **117**, 242), and clearly this must always be the case when the " quantum efficiency " is a true constant. However, Bodenstein and Lütkemeyer (*Z. physikal. Chem.*, 1924, **114**, 208) have recently announced that the rate of union of hydrogen and bromine in the light is proportional to the square root of the energy absorbed when the intensity of the light is kept constant. It is therefore not improbable that the rate of this gaseous reaction is also proportional to the square root of the intensity of the light. We shall show that this assertion of Bodenstein and Lütkemeyer is true without considerable error under suitable conditions. In addition to investigating the dependence of the rate of the change on the intensity of illumination, we have, as in the action of iodine on potassium oxalate, determined the mean life of the postulated catalyst on the concentration of which the rate of the change depends, and the principle of the method employed for this purpose has been the same as that adopted in the case of the other reaction.

EXPERIMENTAL.

The mean life of the catalyst was estimated by determining the hydrogen bromide formed when a mixture of bromine and hydrogen,

of constant composition and enclosed in an appropriate actinometer, was exposed to intermittent light of constant intensity in such a manner that the period during which the mixture was in light bore a constant ratio to the period during which it was in darkness. In these circumstances, the amount of chemical change per unit of radiant energy supplied is dependent on the length of the equal short periods of illumination. From the quantitative relation between the frequency of illumination and the chemical change per unit of energy supplied, the mean life of the catalyst can be determined.

FIG. 1.

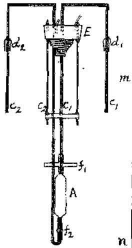
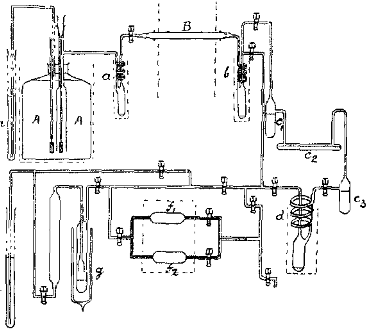


FIG. 2.



The actinometer (Fig. 1) was made from a wide glass tube, *A*, of 2·20 cm. internal diameter and 8 cm. long. The mixed gases entered the actinometer through the capillary tube, c_1, and escaped through the capillary tube c_2. The ground glass joints at d_1 and d_2 served to connect the actinometer with the apparatus employed to analyse its contents at the end of an experiment. During an exposure of the actinometer to light it was immersed in the vapour of boiling dimethylaniline contained in a wide tube of pyrex glass (not shown in the figure) which was kept in position by the stopper *E*. The ends of the glass crosses at f_1 and f_2 touched the sides of the pyrex tube and served to keep the actinometer centrally in the same fixed position.

After the actinometer had been filled, its exposure to intermittent light was accomplished in the following manner. The insolation tube was screened by blackened asbestos board so that no light could

enter it except that which had passed through sectors cut out of a rotating disc of stout cardboard and through a plate-glass window of the same shape as each of the sectors. The disc was provided with eight equal sectors, each being 8 cm. long and situated at a mean distance of 21 cm. from the centre. The sectors were at equal distances from one another, but the angle subtended by each sector at the centre was changed whenever it was desired to alter the ratio of the periods of darkness and illumination. The pyrex jacket was placed as near as possible to the plate-glass window in such a position that the whole of the mixture in the actinometer was equally illuminated. The source of illumination was a 1000-watt incandescent-filament lamp, placed at a horizontal distance of 30 cm. from the reaction vessel. The light from the lamp passed through an aperture of appropriate shape in a large piece of stout sheet-iron which was placed immediately in front of the lamp, the aperture being of such a size that its penumbra was outside the plate-glass window. The current supplied to the lamp was maintained constant with a rheostat worked by hand, and was recorded by a mirror galvanometer. The rotating disc was placed as near as possible to the plate-glass window. The shadow cast by the edge of a sector was quite sharp, but there was some error, which could neither be avoided nor estimated, occasioned by reflexion from the inner wall of the glass bulb of the lamp. The lamp itself was placed in such a position that its incandescent wire subtended in a plane at right angles to the top edge of the window the minimum angle at a point in the actinometer. The disc was kept in rotation by means of a geared motor, and in some of the experiments in which the rotation was slow, by a clock.

The filling of the actinometer with the mixture of hydrogen and bromine was accomplished with the apparatus shown in Fig. 2. The hydrogen was prepared by the electrolysis of an aqueous solution of baryta contained in the large electrolytic cell, A, and was freed from excess of water vapour by passage through a glass worm, a, surrounded by water at a temperature 2° below that of the laboratory. The oxygen was removed by passing the gas through a quartz tube, B, filled with palladised asbestos and heated to redness, and the water formed was condensed in the worm, b, which was kept at the same temperature as a. The moist hydrogen then passed slowly over a large surface of pure liquid bromine contained in glass vessels, three of which are shown diagrammatically at c_1, c_2, and c_3. The hydrogen thus saturated with bromine and almost saturated with water vapour then passed through a long glass worm immersed in a thermostat kept at 12°. The issuing hydrogen which thus contained a constant proportion of water vapour and

bromine, streamed through two almost identical actinometers (shown diagrammatically at f_1 and f_2) which, during the filling, were kept at a constant temperature of 25°. The bromine in the escaping hydrogen was recovered by condensation in a freezing mixture contained in the thermos flask *g*. While the actinometers were being filled, the pressure in the apparatus was kept constant by adjusting the height of the columns of water in *m* and *n*. At the end of a filling, the pressure in the actinometers was reduced to 50 cm. of mercury and the actinometers were then sealed off at the points c_1 and c_2 (Fig. 1). The two almost identical actinometers, thus filled under exactly the same conditions, were subsequently used to compare the rates of formation of hydrogen bromide per unit of radiant energy absorbed under different conditions of illumination.

The analysis of the contents of the actinometers at first presented a difficulty, since the ordinary procedure was found not to be sufficiently accurate. The bromine and hydrogen bromide had to be separated before their amounts were estimated. In principle, the method adopted was to admit into the actinometer a limited amount of pure water and to distil the bromine from the solution of hydrogen bromide and thence into a cooled solution of potassium iodide, the distillation being conducted in such a manner that the hydrobromic acid was retained in the actinometer and in a trap inserted between it and the bulbs containing the potassium iodide solution. The liberated iodine was titrated with standard sodium thiosulphate, and the hydrobromic acid with standard baryta in an atmosphere of hydrogen.

All the bromine used was purified from chlorine and iodine as well as from organic matter by the method recommended by Scott (J., 1913, **103**, 847), and the water used in the electrolytic cell and in the analyses was purified by the following method. Ordinary distilled water was saturated with chlorine and boiled for several hours in a large flask provided with a fused-on reflux condenser. At the end of this operation sufficient potassium bromide was added to interact with the small amount of chlorine still present, and the liberated bromine was removed by boiling under reduced pressure. A few drops of pure potash solution were then added, and after it had been heated, the water was distilled in dust-free air, and the distillate collected in carefully cleaned glass-stoppered bottles.

Discussion.

The experimental results show clearly that if, with a constant intensity of illumination, the disc is made to rotate at different rates, the amount of chemical change in a given time is greater when

the rate of rotation of the disc is greater, the increase in the amount of change being such that it tends to a limit as the rate of rotation is made more rapid. When the disc rotates very slowly, the amount of hydrogen bromide formed in a given time is, of course, independent of the rate of rotation, and becomes the same as that produced by continuous illumination for the same total length of time. The mean life of the postulated catalyst is calculated from the result of a determination of the rate of rotation of the disc for which the mean velocity of chemical change is mid-way between the mean velocities of chemical change previously found for a very rapid and for a very slow rate of rotation of the disc.

That the photochemical union of hydrogen with chlorine and bromine is attributable to ephemeral catalysts (either atoms or active molecules) is now commonly assumed, and the assumption is supported by the fact, now established for the interaction of hydrogen and bromine, that the total amount of chemical change is not solely dependent on the total time of illumination by light of a constant intensity, but alters when the supply of the light is rendered intermittent. In adopting this theory we shall make the following assumptions concerning the catalyst:

(1) For light of a given quality, the rate of formation of the catalyst is proportional to the energy absorbed.

(2) The rate of destruction of the catalyst is the sum of two terms, one being proportional to the first power and the other to the second power of its concentration.

(3) The rate of formation of hydrogen bromide is directly proportional to the concentration of the catalyst.

Taking for granted (1) and (3), we can show that if the rate of destruction of the catalyst is proportional to its concentration, the rate of union of hydrogen and bromine is proportional to the intensity of the light, whereas, if the rate of destruction of the catalyst is proportional to the square of its concentration, the rate of union is proportional to the square-root of the intensity of the light. Thus, on the one hand, if A represents the concentration of the catalyst, I the intensity of the light, t the time, and k and k_2 are constants, the differential equation for the variation of A is

$$dA/dt = kI - k_2A (= 0 \text{ in the steady state}).$$

Wherefore, in the steady state A is proportional to I. Such would be the case if the destruction of the catalyst were caused principally by the impacts of its molecules with molecules of an inhibitor. On the other hand, if

$$dA/dt = kI - k_1A^2 \ (= 0 \text{ in the steady state}),$$

A would be proportional to the square-root of the intensity of the light, and such would be the case if the destruction of the catalyst were caused principally by the impact of two of its molecules.

Our results indicate that the rate of interaction of hydrogen and bromine, for very high intensities of the light, approximates to values which are proportional to the square-root of the intensity, but for low intensities the rate becomes more nearly equal to values proportional to the intensity. Accordingly, we must conclude that the destruction of the catalyst is at the same time both a first- and a second-order reaction, and that the differential equation which gives the time variation of its concentration is

$$dA/dt = kI - k_1A^2 - k_2A \text{ (= 0 in the steady state)} \quad . \quad . \quad (1)$$

Let the units of time, energy, and concentration be so chosen that $k = 1$, $I = 1$, and $A = 1$ in the steady state when the actinometer is fully exposed to light; the values of the constants k_1 and k_2 can then be determined experimentally in the following manner. The actinometer is, in the first place, exposed to the light with the disc rotating very slowly, and the time, t_1, needed for the production of a given amount of hydrogen bromide is determined. Then with the twin actinometer a similar experiment is performed with the disc rotating very rapidly. Let us suppose that the time required for the production of the specified amount of hydrogen bromide is t_2. If α is the ratio to 2π of the sum of the angles subtended at the centre of the disc by all the sectors, then in the first experiment the actinometer was exposed to light of unit intensity for the time αt_1, whilst the result of the second experiment ought obviously to be the same as that of an exposure of the actinometer for a time t_2 to light of intensity α. But since the amount of chemical change is proportional to the product of the concentration of the catalyst and the time of exposure, we must have

$$\alpha t_1 = A_2t_2 \text{ or } A_2 = \alpha t_1/t_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.1)$$

in which A_2 is the approximately constant concentration of the catalyst in the second experiment.

With the new units, equation (1) becomes

$$dA/dt = I - k_1A^2 - k_2A \text{ (= 0 in the steady state)} \quad . \quad . \quad (1.2)$$

In the first experiment, I and A both have by definition the value 1, and in the second experiment I has the value α, and A the value $\alpha t_1/t_2$. On substituting these values in (1.2), we obtain the following two equations from which the values of k_1 and k_2 can be deduced:

$$1 = k_1 + k_2$$

and

$$\alpha = k_1(\alpha t_1/t_2)^2 + k_2(\alpha t_1/t_2)$$

An actual experiment gave for $\alpha t_1/t_2$ the value 0·2391 when α was $\frac{1}{8}$,

from which it follows that k_1 and k_2 are respectively 0·6272 and 0·3728. These were the values of the two constants adopted for the determination of the mean life of the catalyst.

The Determination of the Mean Life of the Catalyst.

In the system of units proposed above, the rate of increase of A becomes $I - k_1A^2 - k_2A_1$, and in this expression I is equal to the rate of production of the catalyst, and $k_1A^2 + k_2A$ to its rate of destruction, per unit volume. The mean life of the catalyst in the steady state is the quotient of A by the rate of production of A, *i.e.*, it is equal to A/I. But under continuous illumination the intensity has been taken as unity, and, under the same conditions, A in the steady state has also been taken as unity. Therefore in the conventional units adopted, the mean life of the catalyst is the unit of time.

Under all conditions the rate of chemical change is proportional to the mean value of A, and therefore, since A is unity when the actinometer is continuously illuminated, its mean value for a given moderate rate of rotation of the disc is the ratio of the rate of chemical change during that moderate rotation to the rate of chemical change under continuous illumination. Experiment therefore supplies us with the information that A has a certain known value when the disc is made to rotate at a known rate measured in seconds, or, in other words, when the equal intervals of illumination have a known value in seconds. It is also possible to calculate what rate of rotation of the disc measured in terms of the new unit of time (*i.e.*, the mean life of a molecule of the catalyst) would result in the same mean value of A. Accordingly, experiment furnishes the value of a rate in seconds, and calculation gives the value of the same rate in mean lives. The numerical ratio of the two values is clearly the value of a mean life in seconds.

The calculation of the rate of rotation of the disc (in mean-life units) which would result in a specified mean value of A is performed in the following way. For the purpose of the calculation it is more convenient to write the differential equation (1.2), which gives the rate of increase of A in the light, in the form $dA/d\tau = I - c_1^2A^2 - c_2A$, in which τ is written for t to indicate that the measurements of time are to be made with a unit equal to the mean life of the catalyst when the intensity of the light is unity, and c_1 and c_2 are constants. When I is taken as unity the solution of the equation is

$$\log_e \frac{\{1 + (c_2/2c_1)^2\}^{\frac{1}{2}} + \{x + c_2/2c_1\}}{\{1 + (c_2/2c_1)^2\}^{\frac{1}{2}} - \{x + c_2/2c_1\}} = 2c_1\{1 + (c_2/2c_1)^2\}^{\frac{1}{2}}\tau + C_1 \quad . \quad (2)$$

where x is substituted for c_1A, and C_1 is the integration constant.

The same symbols being used, the differential equation for the decrease of A in the dark is $dA/d\tau = -c_1{}^2A^2 - c_2A$, of which the solution is

$$\log_e\left\{\frac{x + c_2/c_1}{x}\right\} = c_2\tau + C_2 \quad . \quad . \quad . \quad . \quad (3)$$

where C_2 is the integration constant.

For brevity, (2) is written as $f(x) = \tau$, and (3) as $F(x) = \tau$. If x_1 and x_2 are the values of x at the beginning and end of a period of illumination, and x_2 and x_3 the values of x at the beginning and end of a period of darkness, and τ_1, τ_2, τ_3, and τ_4 the corresponding values of τ

$$\frac{f(x_1) - f(x_2)}{F(x_2) - F(x_3)} = \frac{\tau_2 - \tau_1}{\tau_4 - \tau_3} = \beta$$ (a known constant when the rate of rotation is uniform).

But in the steady state, which is very rapidly approached, x_3 must be equal to x_1 since the increase in x during a period of illumination must then equal its decrease during a period of darkness, and therefore the above equation reduces to

$$f(x_1) + \beta F(x_1) = f(x_2) + \beta F(x_2) \quad . \quad . \quad . \quad . \quad (4)$$

It is easy to show that if any one of the infinite number of possible values of x_2 is introduced into this equation, the resulting equation for x_1 is satisfied by two real values, one of which is, of course, x_2. In other words, for every value of x_2 there is a corresponding value of x_1. Moreover, when x_1 and x_2 are known, the corresponding mean value of x, and also the length of a period of illumination in terms of a mean life of a molecule of the catalyst, can be computed with the aid of equations (2) and (3). By trial, a value of x_2 must be found which gives a mean value of x equal to the experimentally determined value of that constant. Then by a comparison of the calculated period of illumination in mean-life units with the period of illumination expressed in seconds, and deduced from the known rate of rotation of the disc, the mean life in seconds can be calculated.

It is obvious that the required result can also be obtained by graphical methods.

The actual experimental results are tabulated below. In column A the number of the determination is recorded; in B the rates of rotation of the disc in two comparative experiments; in C the ratio of the time of illumination to the sum of the periods of illumination and darkness; in D the times (in minutes) required to effect the same amount of chemical change in two comparative experiments; in E the ratio of these times; and in F and H the respective valnes of the constants k_1 and k_2.

A.	B.	C.	D.	E.	F.	H.
			225 / 174	1·29		
			220 / 176	1·25		
			343 / 265·5	1·29		
I	slow fast	$\frac{1}{2}$ [illegible]	332 / 262	1·27	0·6034	0·3966
			329 / 265·5	1·24		
			353 / 265·5	1·33		
			372 / 267	1·40		
			275 / 174	1·58		
II	fast fast	$\frac{1}{4}$ $\frac{1}{2}$	273 / 174	1·57	0·6701	0·3299
			287 / 174	1·65		
			415 / 174	2·38		
III	fast fast	$\frac{1}{8}$ $\frac{1}{2}$	430 / 174	2·47	0·6961	0·3039
			447 / 174	2·57		
IV	slow fast	$\frac{1}{32}$ $\frac{1}{32}$	910 / 435	2·09	0·5585	0·4415
			424 / 217·5	1·9494		
			416 / 217·5	1·9126		
V	slow fast	$\frac{1}{8}$ $\frac{1}{8}$	409 / 217·5	1·8804	0·6272	0·3728
			415 / 217·5	1·9080		
			mean =	1·9126		
VI	1 rev. in 4 secs. fast	$\frac{1}{8}$ $\frac{1}{8}$	246 / 217·5	1·13		
			238 / 217·5	1·09		
VII	1 rev. in 12·6 secs. fast	$\frac{1}{8}$ $\frac{1}{8}$	369 / 217·5	1·69		
VIII	1 rev. in 11·6 secs. fast	$\frac{1}{8}$ $\frac{1}{8}$	328 / 217·5	1·508		
			314 / 217·5	1·444		
			mean =	1·476		

For the calculation of the mean life of the catalyst the results of the determinations V and VIII were employed, the necessary figures being the mean ratios in column E, namely 1·9126 and 1·476 respectively. The mean life of the catalyst was estimated to be

0·063 second.

Under less intense illumination the mean life would be longer.

It will have been observed that certain approximations, which will affect to some extent the accuracy of the result, have been made.

Conclusion.

If the photochemical interaction of hydrogen and bromine is due to the presence of a catalyst (atoms or activated molecules), the catalyst is capable of existing for an appreciable fraction of a second.

THE LABORATORY,
JESUS COLLEGE, OXFORD. [*Received, May 1st,* 1928.]

CCXXXII.—*The Lupin Alkaloids. Part I.*

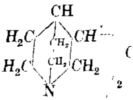
By GEORGE ROGER CLEMO and GRACE CUMMING LEITCH.

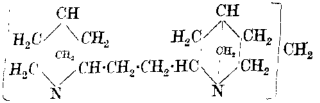
THIS group of alkaloids includes lupinine, $C_{10}H_{19}ON$, sparteine, $C_{15}H_{26}N_2$, lupanine, $C_{15}H_{24}ON_2$, and hydroxylupanine, all of which have been isolated from one or other of the different varieties of lupin seeds. Although numerous chemists have worked on these alkaloids, the present real knowledge of their structures is very scanty indeed. For instance, in spite of the fact that bridged piperidine ring systems have been postulated for these compounds, it appears that there is not a single recorded case of a monocyclic pyridine or piperidine derivative having been definitely obtained from any of them.

Lupinine, present in *Lupinus luteus,* was examined by Willstätter and Fourneau (*Ber.*, 1902, **35**, 1914), who concluded that it contained a primary alcoholic side chain, together with a tertiary nitrogen atom probably common to two rings as in quinuclidine. Recently, Kalle & Co. (D.R.-PP. 386,936 and 396,508) have described the production of chlorolupinine and lupinan, $C_{10}H_{19}N$; but the structural question appears to be still as left by Willstätter in 1902.

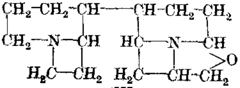
The chief workers on sparteine have been Moureu and Valeur, who advanced the β-diquinuclidylmethane formula (I) for this alkaloid (*Compt. rend.*, 1905, **141**, 117). Germain (*Gazzetta*, 1912, **42**, i, 447) oxidised sparteine with permanganate in phosphoric acid solution

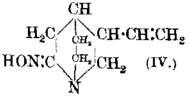
and, obtaining some succinic acid, felt justified in advancing formula (II) for the alkaloid.


(I.)


(II.)

Lupanine occurs in the dextro- and the inactive form in *L. albus* and in the dextro-form in *L. angustifolius,* and the inactive modification can be easily isolated in a pure condition from *L. termis,* which appears to be native to North Africa and Syria. The authors are greatly indebted to Dr. R. G. A. Heathcote, of the Royal School of Medicine, Cairo, for securing the necessary seed and extracting the first batch of *i*-lupanine used in this investigation. The early workers on lupanine include Schmidt (*Arch. Pharm.*, 1897, **235**, 192), who advanced the empirical formula $C_{15}H_{24}ON_2$, and Davis (*ibid.*, p. 199), who proved the absence of a reactive carbonyl or hydroxyl group. Many chemists, including Siebert (*ibid.*, 1891, **229**, 544), Callsen (*ibid.*, 1899, **237**, 577), Soldaini (*Gazzetta*, 1903, **33**, 1428), and Beckel (*Arch. Pharm.*, 1912, **250**, 691), have studied the oxidation of the alkaloid, but except oxalic acid, no oxidation product appears to have been isolated in quantity sufficient for its characterisation. Beckel (*Arch. Pharm.*, 1911, **249**, 329) concluded from titration experiments tbat lupanine is a monoacidic base (see p. 1813). Molander (*Ber. Deut. Pharm. Ges.*, 1921, **31**, 265) subjected tbe alkaloid to drastic treatment with fuming hydrochloric acid at 210°, to fusion with caustic potash, etc., but in all cases the lupanine was recovered almost wholly unchanged. Thoms aud Bergerhoff (*Arch. Pharm.*, 1925, **263**, 1) state that lupanine is recovered when its methylammonium hydroxide is distilled in a vacuum, but that when the alkaloid is distilled with zinc dust a small proportion is changed to give, together with other products, what they describe, mainly from its odour and boiling point, as α-ethylpyridine. On these grounds, they advanced the tentative formula (III) for the alkaloid.


(III.)


(IV.)

The only definitely established facts, however, are that lupanine possesses a very stable, fully saturated ring system with one reactive

tertiary nitrogen atom, and no reactive carbonyl, hydroxyl, or methoxyl groups.

It has now been found that lupanine forms a crystalline *dihydrochloride*. The basic nature of both nitrogen atoms is thus proved, but the result does not exclude the presence of a lactam group >N·CO–, for α-quinuclidones, if they were known, might be expected to be basic from the fact that α-oximino-β-vinylquinuclidine (IV) forms a methiodide (*Ber.*, 1908, **41**, 68). The presence of such a group, whilst explaining why lupanine is very much more soluble in water than deoxylupanine (see p. 1819) or sparteine, is yet difficult to reconcile with its ready solubility in ether and ligroin, with its great stability to acids and alkalis, and with the fact that it cannot be reduced electrolytically. The alternative is that lupanine has an ethereal oxygen atom. Notwithstanding its dibasic character the alkaloid yields only a *monomethiodide* and a *monomethosulphate*, in this respect resembling sparteine. Lupanine methiodide is a stable compound, crystallising unchanged after refluxing with methyl-alcoholic potash, and its quaternary ammonium hydroxide when vacuum-distilled gives lupanine and methyl alcohol. Again, when the methiodide is heated in a vacuum with caustic soda, lupanine is largely regained; but if a mixture of caustic potash and caustic soda is used, the distillate contains, in addition to some lupanine, two methyl-lupanines and a small proportion of simpler bases; and if caustic potash alone is used, the bulk of the distillate consists of simpler bases.

From what follows, it seems probable that the lupanine oxygen atom is in that part of the molecule containing the reactive tertiary nitrogen atom involved in these changes, and if the latter is in a quinuclidine system linked in either the α- or the β-position to the rest of the molecule (see I), more than two methyl-lupanines might be expected to result by the elimination of hydrogen iodide from lupanine methiodide. So far, however, only two methyl-lupanines have been obtained, one of which, *α-methyl-lupanine*, is, remarkably enough, a water-insoluble solid; the *β-compound*, apparently an oil, is easily soluble in water and has only been obtained pure in the form of its crystalline *methiodide*. The α-compound forms a *monohydrochloride* and a *monomethiodide*, and α-methyl-lupanine methylammonium hydroxide, when distilled in a vacuum, is largely converted into an isomeric oil, soluble both in water and in ether (*i.e.*, apparently $\begin{matrix}-CH_2\\ \end{matrix}\!>NMe_2{\cdot}OH \longrightarrow \left(\begin{matrix}-CH_2{\cdot}OH\\ -NMe_2\end{matrix}\right)$, which has not yet been satisfactorily converted into a crystalline methiodide. In addition, a small proportion of α-methyl-lupanine is recovered from the distillate.

When lupanine methiodide is heated in a metal bath with caustic potash, the bulk of the distillate boils below 145°/1 mm. (b. p. of lupanine, 190°/1 mm.) and contains a mixture of bases, three of which have given crystalline derivatives: *e.g.*, a small fraction, b. p. 88—92°/1 mm. (approx.), gives mainly a *picrate* (m. p. 130°) together with a small amount of a second *picrate* which decomposes at 225°, and the fraction, b. p. 127—132°/1 mm., gives a crystalline *picrate* and a *dimethiodide*. Analytical results point to the empirical formula $C_{13}H_{22}N_2$ for the latter *base*, but the question of determining the structure of these degradation products, which are probably derivatives of quinuclidine, is rendered difficult by the fact that the literature contains few references to such compounds, and some of these, as, for instance, the observation by Koenigs (*Ber.*, 1904, **37**, 3250) that the β-ethylquinuclidine methiodide melts between 55—85°, are not very helpful for characterisation purposes. Accordingly, the detailed examination of these bases may have to be supplemented by synthetic work before their structures can be settled.

The possibility that lupanine may be an oxygen derivative of sparteine caused attention to be directed to the action of reducing agents on the base. Prolonged heating at 220° in sealed tubes with fuming hydriodic acid and red phosphorus gave *deoxylupanine*, $C_{15}H_{26}N_2$, but 25% of the lupanine was recovered unchanged. Deoxylupanine is an oil which forms a *monomethiodide* and is sparingly soluble in cold water. The question of its structural relationship to sparteine, which occurs naturally in the lævo-form, is complicated by the fact that it has not been possible to racemise the latter or resolve the former. That no ring change occurs in the preparation of deoxylupanine seems certain from the fact that sparteine can be recovered unchanged after a similar treatment. This fact indicates the presence of the quinuclidine ring system, as β-ethylquinuclidine is stable to hydriodic acid, which decomposes, for example, pyridine and coniine. Deoxylupanine and sparteine, however, differ in some respects in their chemical properties, which points to some structural dissimilarity. For instance, deoxylupanine is much more stable to air than sparteine, and it gives crystalline *mono-* and *di-picrates*, whereas sparteine only forms a crystalline dipicrate. When hydrogen sulphide is passed into an ethereal solution of deoxylupanine containing sulphur in suspension, an orange precipitate results in contrast with the dull red one given by sparteine. Both bases, however, can be readily oxidised to give *isolupanine* and oxysparteine, respectively. *iso*Lupanine resembles lupanine in being very easily soluble in water to give an alkaline solution, and also in organic solvents. It shows no evidence of the

›resence of a reactive carbonyl group, and forms only a *mono-ıethiodide*. Neither lupanine, *iso*lupanine, nor oxysparteine gives › precipitate in the hydrogen sulphide test.

Although, as stated, numerous chemists have unsuccessfully tudied the oxidation of lupanine, it has now been found that it an be easily oxidised by permanganate in acetone solution to give *xylupanine*, $C_{15}H_{22}O_2N_2$. Curiously enough, the action always ends rhen five atomic proportions of oxygen have been used up, and in ddition to oxylupanine a very small amount of another oxidation ›roduct and some oxalic acid are also formed. Oxylupanine is a leliquescent compound giving an aqueous solution which is neutral o litmus. It has no reactive carbonyl, methylene, or hydroxyl ;roup, as judged by its non-reactivity with phenylhydrazine, ›iperonal, and benzoyl chloride, and contains no reactive tertiary ıitrogen atom. It seems certain, however, that *iso*lupanine, ›xylupanine, and oxysparteine are formed by the conversion of ıethylene into carbonyl groups. As these are all non-reactive, the ase for the presence of a carbonyl group in lupanine is strengthened. 'hese facts can be explained if the reactive tertiary nitrogen atom f lupanine is in a quinuclidine ring, which can form at least two someric α-quinuclidones, whose lactam carbonyl groups might be xpected to be non-reactive. On this basis, oxylnpanine might be he αα'-diketo-compound with the nitrogen no longer basic. Against his inference, however, must be put the fact that no oxidation esults similar to the above have been observed with the quinine lkaloids, and further the lupin alkaloids differ completely in ›hysiological action from the latter. Again, it is unlikely that ·quinuclidones would be stable to both alkalis and acids, judging rom the fact that α-oximino-β-vinylquinuclidine (IV) is hydrolysed ›y dilute acids, presumably *via* the α-quinuclidone, to meroquinine.

It is hoped to describe the extension of the work along the afore-ıentioned and cognate lines, and its further bearing on the structural roblem presented by these alkaloids, in a future communication.

EXPERIMENTAL.

i-*Lupanine*.—Crude lupanine sulphate* (80 g.) was dissolved in 'ater (60 c.c.) and made alkaline with caustic potash (160 c.c.; 1·25), and the liberated base was extracted with chloroform and actionated; 41·5 g. of a colourless viscid oil passed over at 185—95°/1 mm. and 2 g. at 195—220°/1 mm. The main fraction uickly crystallised (softened at 85°; m. p. 95°), and after recrystal-sing from acetone (24 c.c.) gave colourless, prismatic plates (30 g.),

* The authors are much indebted to Messrs T. and H. Smith, Ltd., of dinburgh for carrying out the extraction of the seed on a large scale.

m. p. 98—99° (Found : C, 72·7 ; H, 9·8 ; N, 11·4. Calc. for $C_{15}H_{24}ON_2$: C, 72·6 ; H, 9·7 ; N, 11·3%). *i*-Lupanine is very easily *soluble in cold water, giving a strongly* alkaline solution, and in the usual organic solvents.

Lupanine Mono- and Di-hydrochlorides.—The precipitate obtained by passing hydrogen chloride into a solution of lupanine (1 g.) in dry ether (20 c.c.) was collected and dissolved in absolute alcohol (10 c.c.). On dilution with ether (15 c.c.), stout colourless prisms separated, m. p. 185° (decomp.) (Found : C, 55·7 ; H, 7·9 ; Cl, 21·6. $C_{15}H_{24}ON_2$,2HCl requires C, 56·1 ; H, 8·1 ; Cl, 22·1%). The *dihydrochloride* is deliquescent, its aqueous solution being acid to litmus. When it is heated under 1 mm. pressure, decomposition occurs and a sublimate of the very deliquescent crystalline monohydrochloride is formed (Found : Cl, 12·0. Calc. for $C_{15}H_{24}ON_2$,HCl : Cl, 12·4%).

Lupanine Monomethiodide.—When lupanine (as obtained direct by distillation ; 41·5 g.), dissolved in acetone (50 c.c.), was mixed with methyl iodide (20 c.c.), the *methiodide* began to separate almost at once. The mixture was refluxed gently over-night, the crystalline precipitate collected and ground with a small volume of alcohol, and the product (62 g. ; decomp. 246—250°) recrystallised from absolute alcohol, giving stout prisms (51·5 g.), m. p. 258—260° (decomp.), raised to 262—263° by a further crystallisation from alcohol (Found : C, 49·8 ; H, 7·1 ; I, 33·0. $C_{15}H_{24}ON_2$,MeI requires C, 49·2 ; H, 6·9 ; I, 32·6%). The methiodide is very soluble in water and sparingly soluble in absolute alcohol.

Lupanine Monomethosulphate.—Methyl sulphate (1·3 g.) was added to lupanine (2·5 g.) in acetone (5 c.c.), and the solution refluxed over-night. The resulting deliquescent prisms (2·7 g.), m. p. 188°, decomp. 275°, were recrystallised from alcohol (3 c.c.) by dilution with acetone (10 c.c.); m. p. 196° (Found : C, 54·6 ; H, 8·0. $C_{17}H_{30}O_5N_2S$ requires C, 54·5 ; H, 8·0%).

Action of Alkalis on Lupanine Methiodide.—(a) α- *and* β-*Methyllupanines.* The powdered methiodide (2 g.), mixed with caustic potash (1·5 g.) and caustic soda (1·5 g.), was carefully heated under 1 mm. pressure with a free flame, an absorbent charcoal trap being placed between the receiver and the pump. Five such experiments, after the recovery of a small quantity from the trap, gave 5·7 g. of distillate, which set to a buttery mass and on fractionation gave 0·2 g., b. p. up to 145°/1 mm., 1·4 g., b. p. 145—180°/1 mm., and 3·9 g., b. p. 180—190°/1 mm. The last fraction while still an oil was stirred with cold water (25 c.c.), and the resulting colourless solid was collected—filtrate X—washed with a little water, dried on the waterbath, and crystallised (1·5 g.) from a small volume of ligroin (b. p.

60—80°); well-defined, colourless prisms then separated, m. p. 123° (Found: C, 73·7, 73·2; H, 9·7, 9·9; N, 10·2; OMe, 0; *M*, cryoscopic in benzene, 274. $C_{16}H_{26}ON_2$ *requires C*, 73·3; *H*, 9·9; N, 10·7%; *M*, 262). *α-Methyl-lupanine* is readily soluble in the usual organic solvents, but insoluble in water, and its cold acetone solution rapidly decolorises potassium permanganate. From a solution of the base in ether, hydrogen chloride precipitates the *monohydrochloride*, which crystallises from alcohol–ether in flat prisms, m. p. 209° (decomp.) (Found: Cl, 11·2. $C_{16}H_{26}ON_2$,HCl requires Cl, 11·9%).

α-Methyl-lupanine methiodide. The base (3·3 g.) was heated overnight in a sealed tube in the water-bath with methyl alcohol (4 c.c.) and methyl iodide (4 c.c.); the crystalline deposit (4·3 g.), when recrystallised from alcohol, formed stout colourless prisms, m. p. 258° (decomp.) (Found: C, 51·0; H, 7·3; N, 6·9; I, 31·4. $C_{16}H_{26}ON_2$,MeI requires C, 50·5; H, 7·2; N, 6·9; I, 31·4%). The compound was very soluble in cold water, and when distilled with caustic potash in a vacuum gave a mixture of bases apparently similar to those described under (b) below. When, however, the methyl-lupanine methylammonium hydroxide from this methiodide (4·3 g.) was distilled in a vacuum, 2·8 g. of a colourless viscid oil passed over at 190—215°/1 mm., from which 0·3 g. of α-methyl-lupanine was recovered by stirring with water. On fractionating the aqueous filtrate, 2·2 g. of oil passed over at 210—215°/1 mm. (Found: C, 69·9; H, 10·4. $C_{17}H_{30}O_2N_2$ requires C, 69·4; H, 10·2%); this *base* was readily soluble in water and in ether.

The aqueous filtrate X on fractionation gave 2·1 g., b. p. 180—195°/1 mm. This was combined with similar material to give 11 g., and then fractionated into equal first and last fractions. The former slowly set to a buttery mass of lupanine. The latter also deposited a small amount of this base, which was filtered off and the filtrate was refractionated, giving 0·8 g., b. p. up to 188°/1 mm., 2·2 g., b. p. 188°/1 mm., and 1 g., b. p. 188—190°/1 mm. The middle and last fractions were treated in acetone with methyl iodide over-night and the crystalline deposit was then collected and dissolved in absolute alcohol. On cooling, some finely divided, crystalline lupanine methiodide quickly separated. This was removed, and large compact prisms separated from the filtrate over-night. These, after recrystallisation from alcohol, had m. p. 272° (decomp). alone and m. p. below 250° (decomp.) when mixed with lupanine methiodide (Found: C, 51·9; H, 7·2; N, 6·6; I, 31·7. $C_{16}H_{26}ON_2$,MeI requires C, 50·5; H, 7·2; N, 6·9; I, 31·4%). *β-Methyl-lupanine methiodide* is very soluble in water, and more soluble in alcohol than lupanine methiodide.

(b) *The base* $C_{13}H_{22}N_2$. Lupanine methiodide (2 g.), well mixed with caustic potash (3 g.) and heated under 1 mm. pressure at 260°, decomposed, giving a solid mass. The heating at 260° was continued for 15 minutes and the temperature of the bath was then raised to 300°; an oil distilled during the next 5 to 10 minutes. The combined distillates from twelve such experiments (11 g.) were divided into the following fractions: (i) 1·2 g., b. p. 85—112°/1 mm.; (ii) 7·5 g., b. p. 112—132°/1 mm.; (iii) 0·6 g., b. p. 132—150°/1 mm.; (iv) 1·7 g., b. p. up to 170°/1 mm.

When fraction (i) was redistilled, half of it passed over at 88—92°/1 mm. (Found: C, 79·4; H, 10·5; N, 10·8%). This oily *base* was slightly soluble in cold water, giving an alkaline solution, and its cold acetone solution slowly decolorised potassium permanganate. The base (0·5 g.) was boiled with picric acid (0·9 g.) in alcohol (20 c.c.) for 1 minute; the solution was then cooled and decanted from 0·1 g. of a *product* which crystallised from acetic acid in yellow prisms, decomp. 225° after darkening at 215°. The decanted alcoholic solution was partly evaporated, and ether added; lemon-yellow plates then separated, m. p. 130—131° (Found: C, 52·7, 53·0; H, 5·0, 5·2. $C_{18}H_{20}O_7N_4$ requires C, 53·4; H, 4·9%. $C_{17}H_{18}O_7N_4$ requires C, 52·3; H, 4·6%).

When fraction (ii) was redistilled, a large proportion passed over at 127—132°/1 mm.; the portion, b. p. 130°/1 mm., was analysed (Found: C, 76·5; H, 10·4; N, 13·4. $C_{13}H_{22}N_2$ requires C, 75·7; H, 10·7; N, 13·6%). The oil is sparingly soluble in water, and its cold acetone solution decolorises potassium permanganate.

Picrate of the base $C_{13}H_{22}N_2$. An alcoholic solution of the fraction, b. p. 127—132°/1 mm. (1 g.) and picric acid (1·25 g.) was boiled for 1 minute, cooled, and decanted from a small quantity of gum; the *picrate* (1·4 g.) slowly separated in yellow prisms, and melted at 137° after recrystallisation from alcohol (Found: C, 52·3, 52·5; H, 5·8, 6·1. $C_{13}H_{22}N_2,C_6H_3O_7N_3$ requires C, 52·4; H, 5·8%).

Dimethiodide of the base $C_{13}H_{22}N_2$. When the fraction, b. p. 127—132°/1 mm. (1 g.), acetone (3 c.c.), and methyl iodide (1 c.c.) were mixed together, much heat was evolved and an oil separated. After 12 hours, the crystals that had formed were collected, and recrystallised from a solution in alcohol by dilution with acetone, giving almost colourless, compact prisms, m. p. 202°, decomp. 280° (Found: C, 37·3; H, 5·9. $C_{13}H_{22}N_2$,2MeI requires C, 36·9; H, 5·7%).

Deoxylupanine.—Four sealed glass tubes, each containing lupanine (1·25 g.), hydriodic acid (5 c.c.; *d* 2), and red phosphorus (1·25 g.), were heated for 36 hours at 220°, much pressure being developed. The viscid product was heated at 150° under diminished pressure to

remove the excess of hydriodic acid, the residue treated with caustic potash solution (100 c.c.; *d* 1·25), and the liberated oil extracted with chloroform and fractionated; 1·7 g. passed over at 140—170°/1 mm., followed at 170—190° by 0·8 g. which set to a soft crystalline mass of lupanine. The first fraction was seeded with lupanine and left for some days in an ice-chest, the separated lupanine was filtered off, and the filtrate fractionated; the bulk passed over at 145°/1 mm., leaving a small residue of lupanine (Found: C, 77·4; H, 11·2; N, 11·6. $C_{15}H_{26}N_2$ requires C, 76·9; H, 11·1; N, 11·9%). *Deoxylupanine* is sparingly soluble in water, giving an alkaline solution. A deliquescent *dihydrochloride* is formed when hydrogen chloride is passed into an ethereal solution of the base and can be crystallised by slowly diluting its cold alcoholic solution with ether (Found: Cl, 23·0. $C_{15}H_{26}N_2,2HCl$ requires Cl, 23·1%).

Mono- and di-picrates of deoxylupanine. When ethereal solutions containing equal weights of the base and picric acid were mixed, a yellow precipitate of the *monopicrate* was formed, which crystallised from alcohol in well-formed, yellow, hexagonal prisms, m. p. 135° (Found: C, 54·9; H, 6·3. $C_{15}H_{26}N_2,C_6H_3O_7N_3$ requires C, 54·4; H, 6·3%).

The precipitate of the *dipicrate* formed when alcoholic solutions of deoxylupanine (0·25 g.) and picric acid (0·5 g.) were mixed crystallised from alcohol in lemon-yellow needles, m. p. 206—207° (Found: C, 46·7; H, 5·1. $C_{15}H_{26}N_2,2C_6H_3O_7N_3$ requires C, 46·8; H, 4·6%). A mixture with sparteine dipicrate (m. p. 208°) melted at 198—200°.

Deoxylupanine methiodide. The base (1·3 g.) was added to acetone (2 c.c.) and methyl iodide (1 c.c.); after 12 hours, 1·8 g. of the *methiodide* had separated, which crystallised from acetone in colourless plates, m. p. 226° (Found: C, 51·5; H, 7·9. $C_{15}H_{26}N_2,MeI$ requires C, 51·1; H, 7·7%).

iso*Lupanine*.—Deoxylupanine (1·2 g.) on oxidation * gave 0·9 g. of a distillate which crystallised; on recrystallisation from ligroin (b. p. 40—60°) colourless plates, m. p. 113°, were obtained (Found: C, 72·6; H, 9·7. $C_{15}H_{24}ON_2$ requires C, 72·6; H, 9·7%). Mixed with lupanine, the substance melted at 78—80°. When heated in a sealed tube with methyl alcohol and methyl iodide, iso*lupanine* gave a crystalline *monomethiodide*, which separated from alcohol-acetone (1 : 2) in colourless plates, m. p. 208°.

Oxylupanine.—Lupanine (2·5 g.) was dissolved in acetone (30 c.c.), and powdered potassium permanganate (5·3 g.) added during about 4 hours with stirring and cooling in an ice-bath. After being left overnight, the mixture was stirred for ½ hour and filtered, and the sludge extracted with acetone. The solvent was then removed from the

* Details of the method will be published shortly.

filtrate, and the residue * distilled; at about 210°/1 mm., 1·4 g. passed over, which crystallised from acetone in stout colourless prisms, m. p. 123° (Found: C, 69·1; H, 8·3; N, 10·5; *M*, cryoscopic in benzene, 266, 275. $C_{15}H_{22}O_2N_2$ requires C, 68·7; H, 8·4; N, 10·7%; *M*, 262). *Oxylupanine* forms a *chloroplatinate* which crystallises from alcohol in brown prisms, m. p. 232° (decomp.). By means of this salt the value 266 was obtained for the molecular weight of oxylupanine. After being refluxed in alcoholic or acetic acid solution with phenylhydrazine for 24 hours, or in ethereal solution containing benzoyl chloride with sodium bicarbonate in suspension, oxylupanine was recovered unchanged. It could not be condensed with piperonal, and it was also recovered after being heated in acetic acid solution, saturated with hydrogen chloride, for 24 hours at 240°.

One of us (G. R. C.) wishes to thank the Royal Society for grants towards the cost of the seed and of the extraction of the lupanine used in this investigation.

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NEWCASTLE-UPON-TYNE. [*Received, April 11th, 1928.*]

CCXXXIII.—*Neodymium Selenate.*

By JOHN ALBERT NEWTON FRIEND and ALBERT ARTHUR ROUND.

ALTHOUGH selenates of lanthanum (Atomic No. 57), cerium (58), praseodymium (59) and samarium (62) have been described, *neodymium* (60) *selenate* does not appear to have been prepared hitherto. In the course of a search for the "missing" element, No. 61, some fairly pure neodymium magnesium nitrate was prepared by repeated fractionation from certain rare-earth residues. From this the oxalate was precipitated, ignited to oxide, and used in the preparation of the salts described below.

That the oxide thus obtained contained only traces of impurity was proved in several ways. (1) The visible absorption spectrum of a *N*/16-solution of the chloride prepared from the oxide showed close agreement with Rech's data (*Z. wiss. Photochem.*, 1905, **3**, 411). (2) An *X*-ray analysis was made by Messrs. Adam Hilger with a sample of the oxide on a copper target of a Shearer *X*-ray tube, using a Müller *X*-ray spectrograph with calcite crystal. The presence of traces of praseodymium, samarium, and gadolinium was ascertained. Traces of terbium were also present, as shown by the brown tint of

* A trace of a higher oxidation product separates if this residue is redissolved in a small volume of acetone.

the ignited oxide. (3) Chemical analysis was effected by converting a weighed quantity of oxide into sulphate, and pouring the solution into an excess of oxalic acid solution. After 24 hours, the precipitated oxalate was collected on an asbestos filter and estimated by titration with permanganate. This method, which was used by Gooch and Kobayashi (*Amer. J. Sci.*, 1918, **45**, 227) for thorium, appeared to work well with neodymium, the equivalent weight of which was found to be 48·17, 48·30; mean, 48·24, the accepted value for 1925 being 144·27 ÷ 3 or 48·09.

Neodymium Selenate Pentahydrate, $Nd_2(SeO_4)_3,5H_2O$.—Neodymia readily dissolves in aqueous selenic acid. A slight excess was added to the warm acid and, after filtration, the solution was concentrated on the water-bath until a good crop of pink crystals separated from the hot mother-liquor. These were dried between filter-paper and stored over sulphuric acid. Some of the dried salt was heated in a current of dry air, the evolved water being collected in a calcium chloride drying tube. If the heating was gentle, the loss in weight of the salt exactly equalled the gain of the drying tube, indicating that no reduction to selenite or change other than dehydration had taken place; but it was difficult to ensure complete desiccation without slight decomposition of the anhydrous salt [Found: H_2O, 11·47, 11·24; mean, 11·36. $Nd_2(SeO_4)_3,5H_2O$ requires H_2O, 11·15%]. Upon exposure to moist air the dry salt absorbed moisture.

Octahydrate, $Nd_2(SeO_4)_3,8H_2O$.—A solution of neodymium selenate saturated at about 15° was poured into excess of alcohol, whereupon a pink, viscous liquid separated. On agitation with a glass rod the liquid rapidly crystallised to a pink solid, which was coarsely crushed beneath the alcohol, drained, and washed with ether. After drying between filter-paper, the amount of combined water was determined as before [Found: H_2O, 17·19, 17·39, 17·26; mean, 17·28. $Nd_2(SeO_4)_3,8H_2O$ requires H_2O, 16·72. $Nd_2(SeO_4)_3,9H_2O$ requires H_2O, 18·42%]. This hydrate is also formed by prolonged exposure of the saturated solution over concentrated sulphuric acid.

Dodecahydrate, $Nd_2(SeO_4)_3,12H_2O$.—The previous salts readily absorbed moisture in a saturated atmosphere. When the semi-deliquescent mass thus obtained was dried over sulphuric acid, a break occurred in the dehydration-time curve at 23·37% H_2O, indicating the existence of a dodecahydrate (Theory: $12H_2O$, 23·14; $13H_2O$, 24·59%). This hydrate appears to be the one which first separates when a saturated solution is evaporated at room temperature over concentrated sulphuric acid. It rapidly loses water at the ordinary temperature, and prolonged exposure over concentrated sulphuric acid yields the octahydrate. When freed

from adherent saturated solution by pressure between filter-paper, a sample had a water content of 22·2%. This was low for a dodecahydrate, as expected, but higher than the 21·6% required for an undecahydrate.

Neodymium Selenate, $Nd_2(SeO_4)_3$.—The pink *anhydrous* salt is readily obtained by gently heating any of the hydrates in a current of dry air, or at 170—180° for a more prolonged period [Found: Nd_2O_3, 47·29, 45·49; mean, 46·39. $Nd_2(SeO_4)_3$ requires Nd_2O_3, 46·86%]. Although the mean result is in fair agreement with theory, the individual results do not agree as well as one could desire. Probably the second specimen had been imperfectly dehydrated, and the first may have been slightly overheated (see above).

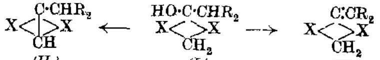
Selenates of all the elements of the cerium sub-group, save No. 61, are now therefore known. The neodymium salt is intermediate in hydrate formation between the praseodymium and samarium salts. For example, the former yields a penta- and an octa-hydrate (Scheele, *Z. anorg. Chem.*, 1898, **17**, 310), the latter yields an octa- and a dodeca-hydrate (Cleve, *Bull. Soc. chim.*, 1874, **21**, 196), and neodymium yields all three. A thorough study of the selenates of this group is in progress with a view to their possible use in the separation of rare-earth mixtures by fractional crystallisation.

THE TECHNICAL COLLEGE, BIRMINGHAM. [*Received, May 23rd*, 1928.]

CCXXXIV.—*The Synthesis of* meso-*Alkyl and* meso-*Aryl Anthracene Derivatives. Part IV.*

By EDWARD DE BARRY BARNETT and JOHN LAURENCE WILTSHIRE.

THE normal product of the action of a Grignard solution on an anthrone is the alkyl or aryl dihydroanthranol (I), from which the alkyl or aryl anthracene (II) or the alkylidene dihydroanthracene (III) is obtained by loss of water (for references, see Part II, J., 1927, 1725):



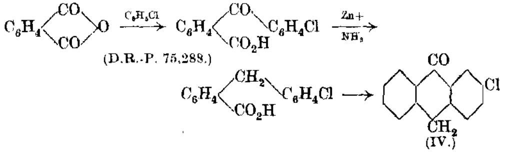
(II.) (I.) (III.)

($X = C_6H_4$ or substituted C_6H_4; R = alkyl, aryl or hydrogen.) The reaction, however, is profoundly affected by the presence of chlorine atoms in α-positions, and when these are present the synthesis either completely breaks down or gives only exceedingly

poor yields except in the cases of magnesium methyl iodide, magnesium phenyl bromide, and magnesium benzyl chloride.

It has now been found that a somewhat similar influence is exerted by a chlorine atom in a β-position, since with 2-chloro-9-anthrone (IV) satisfactory yields of the alkyl anthracene were obtained only with magnesium ethyl bromide and magnesium benzyl chloride, the other magnesium alkyl halides giving extremely poor results. The excellent yield obtained with magnesium ethyl bromide as compared with the very poor yield obtained with magnesium methyl iodide or bromide is interesting, as it is the reverse of what is the case with 1 : 5-dichloroanthrone (Barnett, Cook, and Matthews, *Ber.*, 1926, **59**, 2863).

The 2-chloro-9-anthrone employed in the above experiments was prepared according to the scheme :



(IV.)

It differed from the β-chloroanthrone previously isolated from the reduction of 2-chloroanthraquinone (Barnett and Matthews, J., 1923, **123**, 2554), so the latter must be 3-chloro-9-anthrone.

2-Chloro-9-anthrone (apparently in an impure state) has been described by Meyer and Fischbach (*Ber.*, 1925, **58**, 1251), who obtained it by condensing ω-bromo-*o*-toluoyl bromide with benzene, and oriented it by converting it into a benzanthrone derivative.

EXPERIMENTAL.

4-*Chlorodiphenylmethane-2′-carboxylic Acid.*—4-Chloro-*o*-benzoylbenzoic acid (50 g.) was dissolved in 300 c.c. of ammonia (*d* 0·880) and 150 c.c. of water, 150 g. of zinc dust were added slowly, and finally a few c.c. of copper sulphate solution. Reduction was effected on the water-bath and was complete in about 20 hours. The product was isolated in the usual way and after recrystallisation from alcohol melted at 132° (Found : Cl, 14·1. $C_{14}H_{11}O_2Cl$ requires Cl, 14·4%).

2-*Chloro*-9-*anthrone* (IV).—The above carboxylic acid was added slowly with cooling to concentrated sulphuric acid (3 c.c. per g.) and after it had dissolved the solution was kept at the ordinary temperature for an hour and then poured on ice. The resulting

anthrone after recrystallisation from alcohol melted constantly at 155° and depressed the melting point of the β-chloroanthrone previously described (Barnett and Matthews, *loc. cit.*).

2-Chloro-9-anthranyl acetate was obtained from the above anthrone by the usual acetic anhydride–pyridine method (Barnett and Matthews, J., 1923, **123**, 389). After recrystallisation from alcohol it melted at 143° (Found: Cl, 13·2. $C_{16}H_{11}O_2Cl$ requires Cl 13·1%).

3-Chloro-9-anthranyl acetate was similarly prepared from 3-chloro-9-anthrone. After recrystallisation from alcohol it melted at 146° and depressed the melting point of the above 2-chloro-9-anthranyl acetate (Found: Cl, 13·3%).

Action of Grignard Solutions on 2-Chloro-9-anthrone.—In all cases 7 g. of the finely powdered anthrone were added slowly to the Grignard solution prepared from 2·2 g. of magnesium (3 mols.) and the requisite amount of the halogen compound. After being kept in a freezing mixture for 3 hours, the solution was poured on a mixture of ice and solid ammonium chloride, the washed ethereal layer evaporated to dryness, and the residual oil heated on the water-bath for a short time with acetic acid containing hydrochloric acid The following compounds were obtained, all of which, unless otherwise stated, were recrystallised from methyl or ethyl alcohol and formed pale yellow needles.

2-Chloro-9-methylanthracene, m. p. 84°. Yield, very small (Found: Cl, 15·8. $C_{15}H_{11}Cl$ requires Cl, 15·7%).

2-Chloro-9-ethylanthracene, m. p. 79°. Yield, excellent (Found Cl, 15·0. $C_{16}H_{13}Cl$ requires Cl, 14·8%).

2-Chloro-10-bromo-9-ethylanthracene. By the action of bromine (1 mol.) on the above chloroethylanthracene in carbon disulphide solution. Yellow crystals from benzene–light petroleum; m. p 128° (Found: Cl + Br, 36·1. $C_{16}H_{12}ClBr$ requires Cl + Br, 35·9%)

2-Chloro-9-n-propylanthracene, m. p. 82° (Found: Cl, 14·3 $C_{17}H_{15}Cl$ requires Cl, 13·9%).

2-Chloro-9-benzylanthracene, m. p. 132°. Yield, excellent (Found: Cl, 11·9. $C_{21}H_{15}Cl$ requires Cl, 11·7%).

2-Chloro-10-bromo-9-benzylanthracene. By the action of bromine (1 mol.) on the above chlorobenzylanthracene in carbon disulphide solution. Yellow needles from acetic acid or ethyl acetate; m. p 167° (Found: Cl + Br, 30·4. $C_{21}H_{14}ClBr$ requires Cl + Br, 30·3%)

When the above chlorobenzylanthracene was kept over-night with excess (3 to 4 mols.) of bromine in carbon disulphide solution a substance was obtained (isolated by the addition of light petroleum) which after recrystallisation from benzene–light petroleum formed a cream-coloured powder; this melted and decomposed violently

at about 150°, was difficult to obtain pure, and appeared to be a *dibromide* of 2-chloro-10-bromo-9-benzylanthracene (Found: Cl + Br, 51·4. $C_{21}H_{14}ClBr_3$ requires Cl + Br, 50·9%).

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CCXXXV.—*The Rotatory Dispersion of Derivatives of Tartaric Acid. Part III. Diacetyltartaric Acid and its Esters.*

By PERCY CORLETT AUSTIN.

PREVIOUS work upon diacetyltartaric acid (Austin and Park, J., 1925, **127**, 1926) revealed some anomalies, which could not be properly interpreted at the time. For instance, the lævorotations of a solution of the pure acid in dry acetone were found to be identical with those obtained when the anhydride was mixed in the same solvent with one molecular proportion of water and the mixture had been kept for 16 days until mutarotation was complete; but the presence of increasing amounts of water led to greatly increased lævorotations, a fact which pointed to some further change in structure. Moreover, the values calculated for the velocity coefficients of the hydration of the anhydride indicated that the reaction could be regarded neither as unimolecular nor as bimolecular. Nevertheless, the measurements of rotatory dispersion corresponded well with the values calculated from a simple one-term Drude formula, although the dispersion constant ($\lambda_0^2 = 0{\cdot}0833$) was unusually high. The result was unexpected and the conclusion was drawn that *this acid afforded the first instance of simple dispersion in the tartaric acid series* which was independent of ring formation.

This conclusion was regarded with some suspicion, however, in view of the fact that Patterson's value of the ratio $\alpha_{4358}/\alpha_{5461}$ for the *iso*butyl ester (J., 1916, **109**, 1170) is less than the theoretical minimum for a simple dispersion, *viz.*, 1·57 (compare Lowry and Austin, *Phil. Trans.*, 1922, *A*, **222**, 249), so that the rotatory dispersion of this ester is obviously complex. This ester was therefore prepared, and purified by repeated distillation under low pressures. Since the liquid could not be induced to crystallise, its rotatory dispersion was measured without a solvent in a 4-dcm. tube, whereby an undoubted maximum was detected about 56 Å.U. beyond the blue mercury line. The lower esters of the acid were then prepared by the action of an excess of acetic anhydride on the corresponding esters of tartaric acid, in the presence of a few drops of concentrated

sulphuric acid. The methyl and *iso*propyl esters were easily crystallised, the ethyl ester somewhat less readily, the *n*-propyl ester only with difficulty, and the *n*-butyl and *iso*butyl esters refused to solidify. Readings were therefore taken of the pure liquid *n*-propyl and the two butyl esters and of solutions in the other cases. The *n*- and *iso*-butyl and -propyl esters gave maxima in the visible region, and a solution of the ethyl ester in acetone showed a reversal of sign in the red; but the rotatory dispersion of a solution in acetone of the methyl ester was so nearly simple in the visible region that there was at first some uncertainty as to whether the dispersion was simple or complex. The readings in acetone could not be prolonged beyond 3720 Å.U., and the ester is not sufficiently soluble to be examined in ether; the deviations from a simple formula become marked, however, in the early photographic region. Finally, the complexity of the free acid was established by using dry ether in place of dry acetone as solvent, whereupon it was found that photographic readings could be prolonged considerably farther into the ultra-violet region. The fact that the values of [α] are considerably lower in ether than in acetone may be due to a partial interaction between the acid and acetone to form a definite compound, which would presumably give simple dispersion.

The equations used in Tables I—VIII show that, whereas the dispersion of the other esters is anomalous, that of the methyl ester and of the acid is *complex but normal*, since $\lambda_1^2 < \lambda_2^2$ when $k_1^2 < k_2^2$ (compare Lowry, J., 1915, **107**, 1195). The dispersion constants λ_1^2 and λ_2^2 are 0·0507 and 0·0691, respectively, for the acid and its methyl ester, and 0·0457 and 0·0507 for the other esters. Although, therefore, the rotatory dispersion of most of the esters is obviously anomalous, the dispersion constants of the two terms of Drude's equation differ by an amount corresponding to a separation of only about 114 Å.U. between the characteristic frequencies at 2138 and 2252 Å.U. of the higher esters, and of 377 Å.U. between the characteristic frequencies at 2252 and 2629 Å.U. of the acid and its methyl ester. Under these conditions, as Lowry and Dickson pointed out (J., 1913, **103**, 1075; compare also Hunter, J., 1924, **125**, 1203), it is exceptionally difficult to distinguish between a simple and a complex dispersion, and this distinction would have been quite impossible if the terms had been of similar sign. The rotatory dispersion of the free acid is, indeed, so nearly simple that the calculation of the curves of complex rotatory dispersion which are developed during the hydrolysis of the anhydride (Austin and Park, *loc. cit.*) still holds good without alteration.

It will be seen that the acetyl derivatives give *two* low-frequency terms, where the corresponding hydroxy-compounds are governed

by one term of low frequency and one term of much higher frequency. The increased lævorotations observed on increasing the proportion of water in the mutarotation experiments of diacetyltartaric anhydride (Austin and Park, *loc. cit.*) may therefore be ascribed, as in the case of tartaric acid itself, to an alteration in the equilibrium between two components of opposite sign. The calculation of the true values of the velocity coefficients during mutarotation would then depend on a detailed knowledge, which is not yet available, of the effect of water upon this equilibrium.

An attempt to prolong the region of investigation in the case of diacetyltartaric anhydride by employing ether as solvent was unsuccessful owing to insufficient solubility. The dispersion constant in this case is, however, only 0·0507, and there is no reason to doubt the simple character of the compound on account of the oxygen bridge between the two acid groups.

EXPERIMENTAL.

Preparation of Diacetyltartaric Acid.—In the earlier work great difficulty was experienced in obtaining crystals of the acid which resulted from the slow mutarotation of the anhydride in acetone to which exactly the calculated quantity of water had been added. It is advantageous to concentrate the acetone solution, after mutarotation, by evaporation in a desiccator to a small bulk and to add the residue to boiling benzene, instead of eliminating the acetone. The solubility is thereby greatly increased and much larger crops of crystals can be obtained.

Preparation of the Esters.—These esters have been prepared previously by Anschütz and Pictet (*Ber.*, 1880, **13**, 1175) and by Freundler (*Ann. Chim. Phys.*, 1894, **3**, 454) by the action of acetyl chloride on the tartaric esters. McCrae and Patterson used acetic anhydride with ethyl tartrate and boiled the mixture (J., 1900, **77**, 1098). I have found that the addition of a trace of concentrated sulphuric acid to a mixture of the tartaric ester with a considerable excess of acetic anhydride is sufficient to catalyse the reaction without boiling, since the mixture rapidly becomes hot (compare Chattaway and Parkes, J., 1923, **123**, 663). After standing in the desiccator, the methyl ester soon crystallised, but the ethyl ester crystallised only after several weeks. The methyl ester was washed with ether and recrystallised from the same solvent; m. p. 103°. It is very soluble in acetone. The ethyl ester dissolved readily in both ether and acetone, but could be recrystallised from hot ligroin. As the crystals were slightly coloured, they were melted and the liquid was distilled at 17 mm. pressure; it then boiled at 179°, giving a colourless distillate, which solidified at 67°.

In the remaining cases, the excess of acetic anhydride was carefully distilled off after the mixture had stood for 12 hours, the sulphuric acid neutralised with calcium or barium carbonate, and the distillation continued under reduced pressure. It was found necessary to use flasks with wide side tubes (10—12 mm. diameter) and to heat them in an oil-bath in order to obtain colourless distillates. The first portions were rejected in each case. On cooling, the *iso*propyl ester soon solidified to a mass of crystals, m. p. 31·4°, but the *n*-propyl ester refused to solidify for several months. Eventually crystallisation took place in the polarimeter tube during the course of a set of readings. The substance was then refraction-

TABLE I.

Constants of Diacetyltartaric Acid and its Esters.

	M. p.	B. p.	$d_{4°}^{20°}$.	Liquid examined.	$[a]_D$.	λ_μ Å.U.
Acid	—	—	—	10·83% in acetone	−24·57°	∞
				10·83% in ether	—17·01	∞
Methyl ester	118°	—	—	25% in acetone	−17·87	∞
Ethyl ester	103	179°/17 mm.	—	25% in ether	− 0·50	8531
n-Propyl ester ...	67	181 /10 mm.	1·1114	Supercooled	+11·02	4784
*iso*Propyl ester ..	21·5	167 /11 mm.	—	25% in ether	+ 8·63	5106
n-Butyl ester ...	31·4	205 /15 mm.	1·0823	Liquid ester	+22·20	4821
*iso*Butyl ester ...	—	193 /13 mm.	1·0816	Liquid ester	+67·18	4303

TABLE II.

Rotatory Dispersion of Diacetyltartaric Acid in Ether at 20°.

10·8324 g. $C_8H_{10}O_8$ in 100 c.c. of solution; l = 4 dcm.; $[a] = 2·3077a$.

Simple formula: $[a_1] = \frac{4·235}{\lambda^2 - 0·1009}$ (showing deviations in the ultra-violet).

Complex formula: $[a_2] = \frac{14·380}{\lambda^2 - 0·0507} - \frac{18·229}{\lambda^2 - 0·0691}$.

λ.	[a] obs.	$[a_1]$ calc.	$[a_2]$ calc.	$[a] - [a_2]$.
Li 6708	− 11·82°	− 12·13°	− 11·85°	+0·03°
Li 6104	− 15·35	− 15·59	− 15·39	+0·04
Na 5893	− 17·01	− 17·19	− 17·04	+0·03
Cu 5782	− 18·00	− 18·14	− 18·03	+0·03
Hg 5780	− 18·05	− 18·16	− 18·05	±0·00
Cu 5700	− 18·83	− 18·91	− 18·82	−0·01
Ag 5469	− 21·35	− 21·37	− 21·37	+0·02
Hg 5461	− 21·46	− 21·46	− 21·46	±0·00
Cu 5219	− 24·76	− 24·70	− 24·81	+0·05
Ag 5209	− 24·92	− 24·48	− 24·96	+0·04
Cu 5154	− 25·87	− 25·71	− 25·85	−0·02
Cu 5105	− 26·70	− 26·52	− 26·68	−0·02
Cd 5086	− 27·05	− 26·84	− 27·01	−0·04
Li 4602	− 38·54	− 38·19	− 38·49	−0·05
Hg 4359	− 47·54	− 47·53	− 47·54	±0·00
Fe 4132	− 59·4	− 60·6	− 59·6	+0·2
Fe 3860	− 81·9	− 88·0	− 81·9	±0·0
Fe 3767	− 92·3	−103·3	− 92·7	+0·4
Fe 3720	− 99·2	−113·0	− 99·1	−0·1
Fe 3650	−109·6	−130·6	−110·0	+0·4
Fe 3609	−117·7	−144·3	−117·3	−0·4
Fe 3581	−122·3	−154·9	−122·8	+0·5
Fe 3542	−131·5	−172·4	−131·1	−0·4
Fe 3498	−140·8	−197·3	−141·6	+0·8

ated and crystallised by seeding. It melted at 21·5°,* but observations could be made with the supercooled liquid. For the purpose of comparison with older results, the observed melting points, boiling points, densities, and specific rotations for the sodium line are summarised in Table I, which also shows the wave-lengths λ_μ of maximum rotations.

The remaining tables show the observed and the calculated values of the specific rotations over a wide range of wave-lengths. *The concentration of the solution of diacetyltartaric acid in ether (Table II) is the same as that in acetone, given in Part II. 10·8334 G. of the acid are equivalent to 10·0 g. of the anhydride.*

TABLE III.

Rotatory Dispersion of Methyl Diacetyltartrate in Acetone at 20°.

25 g. of $C_{10}H_{14}O_8$ in 100 c.c. of solution; l = 4 dcm.; $a = [a]$.

Complex formula : $[a_1] = \dfrac{10\cdot200}{\lambda^2 - 0\cdot0507} - \dfrac{14\cdot551}{\lambda^2 - 0\cdot0691}$.

	λ.	[a] obs.	[a₁] calc.	[a]−[a₁].		λ.	[a] obs.	[a₁] calc.	[a]−[a₁].
Li	6708	−12·64°	−12·66°	+0·02°	Cu	5105	−27·34°	−27·39°	+0·05°
Cd	6438	−14·06	−14·09	+0·03	Cd	5086	−27·74	−27·71	−0·03
Li	6104	−16·28	−16·26	−0·02	Cd	4800	−33·39	−33·45	+0·06
Na	5893	−17·87	−17·92	+0·05	Cd	4678	−36·56	−36·52	−0·04
Cu	5782	−18·88	−18·90	+0·02	Li	4602	−38·80	−38·66	−0·14
Hg	5780	−18·93	−18·92	−0·01	Hg	4359	−47·14	−47·14	±0·00
Cu	5700	−19·68	−19·69	+0·01	Fe	4132	−58·0	−58·2	+0·2
Ag	5469	−22·25	−22·20	−0·05	Fe	4046	−63·5	−63·6	+0·1
Hg	5461	−22·30	−22·30	±0·00	Fe	3978	−68·5	−68·4	−0·1
Cu	5219	−25·60	−25·57	−0·03	Fe	3879	−76·5	−76·6	+0·1
Ag	5209	−25·69	−25·72	+0·03	Fe	3860	−78·5	−78·4	−0·1
Cu	5154	−26·55	−26·58	+0·03	Fe	3720	−93·5	−93·7	+0·2

TABLE IV.

Rotatory Dispersion of Ethyl Diacetyltartrate in Ether at 20°.

25 g. of $C_{12}H_{18}O_8$ in 100 c.c. of solution; l = 4 dcm.

Complex formula : $a = [a] = \dfrac{86\cdot666}{\lambda^2 - 0\cdot0457} - \dfrac{85\cdot400}{\lambda^2 - 0\cdot0507}$.

	λ.	[a] obs.	[a₁] calc.	[a]−[a₁].		λ.	[a] obs.	[a₁] calc.	[a]−[a₁].
Li	6708	+0·49°	+0·49°	±0·00°	Cu	5105	− 3·56°	− 3·58°	+0·02°
Cd	6438	+0·24	+0·25	−0·01	Cd	5806	− 3·71	− 3·70	−0·01
Li	6104	−0·19	−0·19	±0·00	Cd	4800	− 5·99	− 6·01	+0·02
Na	5893	−0·58	−0·58	±0·00	Cd	4678	− 7·36	− 7·36	±0·00
Cu	5782	−0·83	−0·83	±0·00	Li	4602	− 8·35	− 8·34	−0·01
Hg	5780	−0·84	−0·84	±0·00	Hg	4359	−12·47	−12·47	±0·00
Cu	5700	−1·05	−1·04	−0·01	Fe	4132	−18·30	−18·30	+0·00
Ag	5469	−1·78	−1·79	+0·01	Fe	4046	−21·30	−21·29	−0·01
Hg	5461	−1·82	−1·82	±0·00	Fe	3978	−24·00	−24·03	+0·03
Cu	5219	−2·90	−2·91	+0·01	Fe	3879	−28·80	−28·77	−0·03
Ag	5209	−2·99	−2·97	−0·02	Fe	3799	−33·40	−33·41	+0·01
Cu	5154	−3·29	−3·28	−0·01	Fe	3720	−38·90	−38·89	−0·01

* *Freundler gives 31° as the m. p.*, but this could not be confirmed.

TABLE V.

Rotatory Dispersion of n-*Propyl Diacetyltartrate at* 20°.

$d^{20°} = 1{\cdot}1114$; $[a] = 0{\cdot}4499a$; $l = 4$ dcm.

Complex formula : $[a_1] = \frac{87{\cdot}828}{\lambda^2 - 0{\cdot}0457} - \frac{83{\cdot}099}{\lambda^2 - 0{\cdot}0507}$.

	λ.	[a] obs.	[a₁] calc.	[a]−[a₁].		λ.	[a] obs.	[a₁] calc.	[a]−[a₁].
Li	6708	+ 9·13°	+ 9·12°	+0·01°	Cu	5154	+12·70°	+12·71°	−0·01°
Cd	6438	+ 9·72	+ 9·73	−0·01	Cu	5105	+12·80	+12·79	+0·01
Li	6104	+10·51	+10·52	−0·01	Cd	5086	+12·81	+12·82	−0·01
Na	5893	+11·02	+11·03	−0·01	Cd	4800	+13·09	+13·08	+0·01
Cu	5782	+11·31	+11·31	0·00	Cd	4678	+13·05	+13·04	+0·01
Hg	5780	+11·31	+11·31	±0·00	Li	4602	+12·93	+12·94	−0·01
Cu	5700	+11·50	+11·51	0·01	Hg	4359	+12·10	+12·10	±0·00
Ag	5469	+12·08	+12·06	+0·02	*Fe*	*4062*	+ *9·18*	+ *9·17*	*+0·01*
Hg	5461	+12·08	+12·08	±0·00	*Fe*	*4045*	+ *8·91*	+ *8·89*	*+0·02*
Cu	5219	+12·59	+12·59	±0·00	*Fe*	*4005*	+ *8·19*	+ *8·21*	*−0·02*
Ag	5209	+12·62	+12·61	+0·01	*Fe*	*3957*	+ *7·24*	+ *7·26*	*−0·02*

TABLE VI.

Rotatory Dispersion of iso*Propyl Diacetyltartrate in Ether at* 20°.

25 g. of $C_{14}H_{22}O_8$ in 100 c.c. of solution; $l = 4$ dcm.

Complex formula : $a = [a_1] = \frac{91{\cdot}392}{\lambda^2 - 0{\cdot}0457} - \frac{87{\cdot}310}{\lambda^2 - 0{\cdot}0507}$.

	λ.	[a] obs.	[a₁] calc.	[a]−[a₁].		λ.	[a] obs.	[a₁] calc.	[a]−[a₁].
Li	6708	+7·40°	+7·39°	+0·01°	Cu	5154	+9·30°	+9·32°	−0·02°
Cd	6438	+7·80	+7·81	−0·01	Cu	5105	+9·30	+9·32	−0·02
Li	6104	+8·34	+8·34	±0·00	Cd	5086	+9·32	+9·31	+0·01
Na	5893	+8·63	+8·65	−0·02	Cd	4800	+8·96	+8·95	+0·01
Cu	5782	+8·83	+8·81	+0·02	Cd	4678	+8·60	+8·58	+0·02
Hg	5780	+8·81	+8·81	±0·00	Li	4602	+8·25	+8·26	−0·01
Cu	5700	+8·95	+8·92	+0·03	Hg	4359	+6·57	+6·57	±0·00
Ag	5469	+9·15	+9·17	−0·02	*Fe*	*4062*	*+2·20*	*+2·20*	*±0·00*
Hg	5461	+9·18	+9·18	±0·00	*Fe*	*4005*	*+0·90*	*+0·89*	*+0·01*
Cu	5219	+9·30	+9·32	−0·02	*Fe*	*3967*	*−0·10*	*−0·09*	*−0·01*
Ag	5209	+9·31	+9·32	−0·01					

TABLE VII.

Rotatory Dispersion of n-*Butyl Diacetyltartrate at* 20°.

$d^{20°}_{4°} = 1{\cdot}0823$; $l = 2$ dcm.; $[a] = 0{\cdot}462a$.

Complex formula : $[a_1] = \frac{83{\cdot}803}{\lambda^2 - 0{\cdot}0457} - \frac{79{\cdot}374}{\lambda^2 - 0{\cdot}0507}$.

	λ.	[a] obs.	[a₁] calc.	[a]−[a₁].		λ.	[a] obs.	[a₁] calc.	[a]−[a₁].
Li	6708	+ 8·50°	+ 8·49°	+0·01°	Cu	5154	+11·75°	+11·74°	+0·01°
Cd	6438	+ 9·05	+ 9·05	±0·00	Cu	5105	+11·80	+11·81	−0·01
Li	6104	+ 9·78	+ 9·77	+0·01	Cd	5806	+11·83	+11·84	−0·01
Na	5893	+10·26	+10·25	+0·01	Cd	4800	+12·02	+12·02	±0·00
Cu	5782	+10·49	+10·50	−0·01	Cd	4678	+11·96	+11·95	+0·01
Hg	5780	+10·51	+10·50	+0·01	Li	4602	+11·85	+11·83	+0·02
Cu	5700	+10·68	+10·68	±0·00	Hg	4359	+10·94	+10·95	−0·01
Ag	5469	+11·18	+11·18	±0·00	*Fe*	*4085*	+ *8·32*	+ *8·36*	*−0·04*
Hg	5461	*+11·19*	*+11·19*	±0·00	*Fe*	*4046*	+ *7·85*	+ *7·77*	*+0·08*
Cu	5219	+11·63	+11·64	−0·01	*Fe*	*3997*	+ *6·93*	+ *6·93*	*±0·00*
Ag	5209	*+11·63*	*+11·66*	−0·03	*Fe*	*3971*	+ *6·47*	+ *6·43*	*+0·04*

TABLE VIII.

Rotatory Dispersion of iso*Butyl Diacetyltartrate at* 20°.

$d_{4°}^{20°} = 1{\cdot}0816$; $l = 4$ dcm.; $[\alpha] = 0{\cdot}2311\alpha$.

Complex formula : $[\alpha_1] = \frac{85{\cdot}584}{\lambda^2 - 0{\cdot}0457} - \frac{79{\cdot}557}{\lambda^2 - 0{\cdot}0507}$.

	λ.	[α] obs.	[α₁] calc.	[α]−[α₁].		λ.	[α] obs.	[α₁] calc.	[α]−[α₁]
Li	6708	+12·46°	+12·44°	+0·02°	Cu	*5106*	+19·22°	+19·22°	±0·00°
Cd	6438	+13·37	+13·38	−0·01	Cd	5086	+19·32	+19·32	±0·00
Li	6104	+14·65	+14·66	−0·01	Cd	4800	+20·64	+20·64	±0·00
Na	5893	+15·53	+15·54	−0·01	Cd	4678	+21·17	+21·15	+0·02
Cu	5782	+16·03	+16·02	+0·01	Li	4602	+21·38	+21·42	−0·04
Hg	5780	+16·04	+16·03	+0·01	Hg	4359	+21·97	+21·97	±0·00
Cu	*5700*	*+16·38*	*+16·39*	*−0·01*	*Fe*	*4186*	*+21·87*	*+21·91*	*−0·04*
Ag	5469	+17·48	+17·47	*+0·01*	*Fe*	*4177*	*+21·84*	*+21·82*	*+0·02*
Hg	5461	+17·50	+17·50	±0·00	*Fe*	*4155*	*+21·77*	*+21·78*	*−0·01*
Cu	5219	+18·66	+18·67	−0·01	*Fe*	*4132*	*+21·73*	*+21·70*	*+0·03*
Ag	5209	+18·72	+18·72	±0·00	*Fe*	*4076*	*+21·45*	*+21·43*	*+0·02*
Cu	5154	+19·00	+18·99	+0·01					

The readings were made with a Bellingham and Stanley polarimeter, the cost of which was defrayed by a grant for which I am indebted to the Government Grant Committee of the Royal Society.

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CCXXXVI.—*The Rotatory Dispersion of Derivatives of Tartaric Acid. Part IV. Propyl and Butyl Tartrates.*

By PERCY CORLETT AUSTIN.

SINCE the investigation of the esters of diacetyltartaric acid recorded in Part III (preceding paper) involved the preparation of *n*-propyl, *iso*propyl, *n*-butyl, and *iso*butyl tartrates, measurements of the rotatory dispersions of these esters were made in order that they might be compared with values previously obtained by Lowry and Abram for methyl tartrate (J., 1915, **107**, 1187) and by Lowry and Cutter for the ethyl ester (J., 1922, **121**, 542). It has been found that in every case the rotatory dispersion is both complex and anomalous, but although the same dispersion constants are used throughout the series, no simple relation appears to exist between the rotation constants. These are recorded in Table I, which also shows the melting points, boiling points, and densities, where ascertained, and the wave-lengths λ_μ calculated for maximum rotations. For comparison, the published values for the methyl and ethyl esters are included. The value of λ_μ for methyl tartrate is exceptionally high.

TABLE I.

Constants of the Esters at 20°.

Ester.	M.p.	B. p.	$d_{4^\circ}^{20^\circ}$.	k_1.	k_2.	λ_μ, Å.U.	Liquid examined.
Methyl	48° & 61·5°*	—	—	22·576	22·079	15436	Supercooled.
Ethyl	18·7	—	1·2028	25·005	20·678	5629	,,
n-Propyl	—	177°/17 mm.	1·1186	22·139	17·124	4957	Pure ester.
*iso*Propyl	—	152°/12 mm.	1·1136	27·680	20·140	4548	,,
n-Butyl	21·8	182°/11 mm.	1·0909	21·436	16·687	5009	Supercooled.
isoButyl	*66*	*171°/11 mm.*	—	*24·985*	*18·741*	*5374*	*25% in ether.*

* *Dimorphous.*

Preparation of the Esters.—The preparation of the propyl esters was more troublesome than that of the butyl esters, since in the latter case the boiling points of the alcohols are sufficiently high to enable one to eliminate the water produced by slowly distilling off a constant-boiling mixture of the alcohol and water through a long fractionating column. When the propyl alcohols were used, it was necessary to use a dehydrating agent. Hydrogen chloride was first used, but in order to avoid possible contamination of the final product with chlorinated compounds (compare Lowry and Cutter, *loc. cit.*), calcium chloride was substituted later. The solubility of calcium chloride in the alcohol renders its subsequent removal troublesome, but fairly satisfactory yields could be obtained. The powdered tartaric acid dissolved much more rapidly in *n*-butyl than in *iso*butyl alcohol. The esters were carefully distilled and fractionated under low pressure. An oil-bath was used for heating the distillation flasks. This was particularly necessary in the case of *iso*propyl tartrate, which decomposes somewhat readily.

The results are in the following tables. The rotations are all positive, except the one case recorded.

TABLE II.

Rotatory Dispersion of n-*Propyl Tartrate at* 20°.

$d_{4^\circ}^{20^\circ} = 1{\cdot}1186$; $l = 2$ dcm.; $[\alpha] = 0{\cdot}447\alpha$.

$$\text{Complex formula}: [\alpha_1] = \frac{22{\cdot}139}{\lambda^2 - 0{\cdot}030} - \frac{17{\cdot}124}{\lambda^2 - 0{\cdot}056}.$$

λ.	[α] obs.	[α₁] calc.	[α] − [α₁].	λ.	[α] obs.	[α₁] calc.	[α] − [α₁].
Li 6708	9·26°	9·25°	+0·01°	Cd 5086	12·32°	12·33°	−0·01°
Cd 6438	9·80	9·81	−0·01	Cd 4800	12·28	12·29	−0·01
Li 6104	10·55	10·54	+0·01	Cd 4678	12·07	12·08	−0·01
Na 5893	10·99	10·99	±0·00	Li 4602	11·86	11·87	−0·01
Cu 5782	11·23	11·22	+0·01	Hg 4359	10·58	10·58	±0·00
Hg 5780	11·27	11·27	±0·00	*Fe 4132*	*8·05*	*8·06*	*−0·01*
Cu 5700	11·38	11·39	−0·01	*Fe 4046*	*6·57*	*6·59*	*−0·02*
Ag 5469	11·83	11·83	±0·00	*Fe 3978*	*5·14*	*5·15*	*−0·01*
Hg 5461	11·85	11·85	±0·00	*Fe 3956*	*4·65*	*4·63*	*+0·02*
Cu 5219	12·20	12·20	±0·00	*Fe 3930*	*3·93*	*3·96*	*−0·03*
Ag 5209	12·21	12·21	±0·00	*Fe 3879*	*2·46*	*2·51*	*−0·05*
Cu 5154	12·29	12·27	+0·02	*Fe 3856*	*1·79*	*1·78*	*+0·01*
Cu 5105	12·31	12·31	±0·00	*Fe 3799*	*−0·22*	*−0·22*	*±0·00*

TABLE III.

Rotatory Dispersion of iso*Propyl Tartrate at* 20°.

$d_{4^\circ}^{20^\circ} = 1{\cdot}1136$; $l = 2$ dcm.; $[\alpha] = 0{\cdot}449\alpha$.

Complex formula: $[\alpha_1] = \frac{27{\cdot}680}{\lambda^2 - 0{\cdot}030} - \frac{20{\cdot}140}{\lambda^2 - 0{\cdot}056}$.

λ.	[α] obs.	[α₁] calc.	[α]−[α₁].	λ.	[α] obs.	[α₁] calc.	[α]−[α₁].
Li 6708	14·79°	14·79°	±0·00°	Cd 5086	21·69°	21·68°	+0·01°
Cd 6438	15·79	15·81	−0·02	Cd 4800	22·64	22·64	±0·00
Li 6104	17·17	17·18	−0·01	Cd 4678	22·90	22·90	±0·00
Na 5893	18·09	18·10	−0·01	Li 4602	23·02	22·99	+0·03
Cu 5782	18·59	18·59	±0·00	Hg 4359	22·70	22·70	±0·00
Hg 5780	18·59	18·60	−0·01	*Fe 4132*	*21·10*	*21·15*	*−0·05*
Cu 5700	18·97	18·96	+0·01	*Fe 4045*	*19·98*	*20·01*	*−0·03*
Ag 5469	19·99	20·01	−0·02	*Fe 3971*	*18·72*	*18·72*	±0·00
Hg 5461	20·05	20·05	±0·00	*Fe 3872*	*16·39*	*16·38*	*+0·01*
Cu 5219	21·13	21·12	+0·01	*Fe 3807*	*14·37*	*14·37*	±0·00
Ag 5209	21·17	21·17	±0·00	*Fe 3790*	*13·78*	*13·77*	+0·01
Cu 5154	21·40	21·40	±0·00	*Fe 3749*	*12·21*	*12·18*	*+0·03*
Cu 5105	21·60	21·60	±0·00				

TABLE IV.

Rotatory Dispersion of n-*Butyl Tartrate at* 20°.

Supercooled to 20°; setting point 21·8°; $d_{4^\circ}^{20^\circ} = 1{\cdot}0909$; $l = 4$ dcm.; $[\alpha] = 0{\cdot}2292\alpha$.

Complex formula: $[\alpha_1] = \frac{21{\cdot}436}{\lambda^2 - 0{\cdot}030} - \frac{16{\cdot}687}{\lambda^2 - 0{\cdot}056}$.

λ.	[α] obs.	[α₁] calc.	[α]−[α₁].	λ.	[α] obs.	[α₁] calc.	[α]−[α₁].
Li 6708	8·66°	8·68°	−0·02°	Cu 5105	11·39°	11·40°	−0·01°
Cd 6438	9·22	9·20	+0·02	Cd 5086	11·44	11·41	+0·03
Li 6104	9·85	9·86	−0·01	Cd 4800	11·35	11·28	+0·07
Na 5893	10·26	10·27	−0·01	Cd 4678	11·00	11·04	−0·04
Cu 5782	10·46	10·48	−0·02	Li 4602	10·80	10·80	±0·00
Hg 5780	10·48	10·48	±0·00	Hg 4359	9·44	9·44	±0·00
Cu 5700	10·63	10·63	±0·00	*Fe 4132*	*6·87*	*6·87*	±0·00
Ag 5469	11·04	11·02	+0·02	*Fe 4064*	*5·72*	*5·73*	*−0·01*
Hg 5461	11·03	11·03	±0·00	*Fe 4046*	*5·39*	*5·39*	*±0·00*
Cu 5219	11·33	11·32	+0·01	*Fe 3978*	*3·91*	*3·94*	*−0·03*
Ag 5209	11·32	11·33	−0·01	*Fe 3879*	*1·26*	*1·30*	*−0·04*
Cu 5154	11·35	11·37	−0·02	*Fe 3860*	*0·69*	*0·71*	*−0·02*

TABLE V.

Rotatory Dispersion of iso*Butyl Tartrate in Ether at* 20°.

25 g. $C_{12}H_{22}O_6$ in 100 c.c. of solution; $l = 4$ dcm.; $[\alpha] = \alpha$.

Complex formula: $[\alpha_1] = \frac{24{\cdot}985}{\lambda^2 - 0{\cdot}030} - \frac{18{\cdot}741}{\lambda^2 - 0{\cdot}056}$.

λ.	α=[α] obs.	[α₁] calc.	[α]−[α₁].	λ.	α=[α] obs.	[α₁] calc.	[α]−[α₁].
Li 6708	11·92°	11·92°	±0·00°	Cu 5105	16·76°	16·75°	+0·01°
Cd 6438	12·69	12·70	−0·01	Cd 5086	16·80	16·79	+0·01
Li 6104	13·72	13·73	−0·01	Cd 4800	17·22	17·21	+0·01
Na 5893	14·43	14·41	+0·02	Cd 4678	17·22	17·22	±0·00
Cu 5782	14·77	14·76	+0·01	Li 4602	17·16	17·14	+0·02
Hg 5780	14·77	14·77	±0·00	Hg 4359	16·30	16·30	±0·00
Cu 5700	15·00	15·03	−0·03	*Fe 4177*	*14·70*	*14·75*	*−0·05*
Ag 5469	15·76	15·76	±0·00	*Fe 4045*	*12·80*	*12·84*	*−0·04*
Hg 5461	15·78	15·78	±0·00	*Fe 3978*	*11·50*	*11·53*	*−0·03*
Cu 5219	16·49	16·47	+0·02	*Fe 3878*	*9·00*	*8·99*	*+0·01*
Ag 5209	16·50	16·50	±0·00	*Fe 3860*	*8·50*	*8·44*	*+0·06*
Cu 5154	16·74	16·74	±0·00				

The readings were made with an instrument, the cost of which was defrayed by a grant from the Government Grant Committee of the Royal Society, to whom I am indebted.

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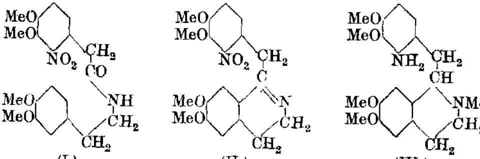
CCXXXVII.—*Synthetical Experiments on the Aporphine Alkaloids. Part III. A Synthesis of Corytuberine Dimethyl Ether.*

By JOHN MASSON GULLAND and ROBERT DOWNS HAWORTH.

THE method described in Parts I and II of this series (this vol., pp. 581, 1132) has now been applied to the synthesis of 3 : 4 : 5 : 6-tetramethoxyaporphine (IV), the *d*-form of which is identical with *corytuberine dimethyl ether (corydine and isocorydine monomethyl ether)*.

2'-*Nitro*-3' : 4'-*dimethoxyphenylaceto*-β-3 : 4-*dimethoxyphenylethylamide* (I) was prepared from 2-nitro-3 : 4-dimethoxyphenylacetyl chloride and β-veratrylethylamine, and converted into 2'-*nitro*-6 : 7 : 3' : 4'-*tetramethoxy*-1-*benzyl*-3 : 4-*dihydroisoquinoline* (II) by the action of phosphorus pentachloride. This pale yellow, crystalline base, which forms a crystalline *hydrochloride*, was converted into its *methiodide*, and the latter was reduced with zinc dust and hydrochloric acid to 2'-*amino*-6 : 7 : 3' : 4'-*tetramethoxy*-1-*benzyl*-2-*methyltetrahydroisoquinoline* (III). This oily base, which yields a crystalline *dihydrochloride*, diazotises readily and the diazonium salts couple with β-naphthol in alkaline solution.

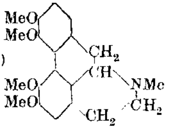


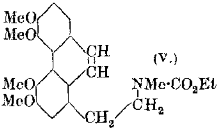
(I.) (II.) (III.)

The base (III) was diazotised in a mixture of methyl alcohol and sulphuric acid and converted into 3 : 4 : 5 : 6-*tetramethoxyaporphine* (IV) by warming. This *dl*-base is a pale yellow oil from which a crystalline *methiodide* has been prepared. The *dl*-base (IV) was resolved by means of *d*-tartaric acid, and 1-*corytuberine dimethyl ether* d-*bitartrate* was thus obtained in crystalline

condition. *d*-Corytuberine dimethyl ether *l*-bitartrate was then prepared by liberating the base from the mother-liquors and combining it with *l*-tartaric acid. The *d*- and *l*-bases were obtained from the bitartrates in the form of oils. These gave the colour reactions described by Gadamer (*Arch. Pharm.*, 1911, **249**, 547) for the oily corytuberine dimethyl ether, which he prepared by methylating naturally occurring *d*-corytuberine.

As we do not possess a sample of the natural product, direct comparison has not been possible, but the melting points, solubilities, and rotation values of the *l*-bitartrate and the methochloride of the synthetical *d*-base are in close agreement with those which Gadamer (*loc. cit.*) records for the corresponding derivatives of the *d*-base obtained from natural sources. Further, the optically inactive carbethoxycorytuberine dimethyl ether (V), prepared by the action of sodium hydroxide and ethyl chloroformate on the synthetical *d*- or *dl*-base, appears to be identical with the product obtained by Osada (*Arch. Pharm.*, 1924, **262**, 501) in a similar manner from the *d*-base of natural origin.

(IV.) 

 (V.)

This synthesis confirms the structure which Gadamer (*loc. cit.*) suggested for corytuberine dimethyl ether (corydine and *iso*corydine monomethyl ether), and we hope to determine by analogous syntheses the positions of the phenolic hydroxyl groups in these alkaloids.

Experimental.

2'-Nitro-3' : 4'-dimethoxyphenylaceto-β-3 : 4-dimethoxyphenylethylamide (I).—A benzene solution of 2-nitro-3 : 4-dimethoxyphenylacetyl chloride (prepared from 5 g. of acid as described in this vol., p. 1134) and β-veratrylethylamine (3·7 g.) was cooled and shaken with a slight excess of 15% sodium hydroxide solution. The benzene layer was washed with dilute hydrochloric acid and dried with sodium sulphate, and the solvent removed. The residual oil was dissolved in a little methyl alcohol (in which it is very soluble) and mixed with ether, the alcohol was removed by washing with water, and the ether was dried and allowed to evaporate slowly; the *amide* separated in almost colourless nodules, m. p. 64—65°, containing solvent of crystallisation which is lost at 100° (Found in material dried at 110°: C, 60·2; H, 6·2. $C_{20}H_{24}O_7N_2$ requires

C, 59·6; H, 5·7%). This amide is very soluble in the usual organic solvents with the exception of light petroleum.

2'-Nitro-6 : 7 : 3' : 4'-tetramethoxy-1-benzyl-3 : 4-dihydroisoquinoline (II).—A solution of the amide (I) (5 g.), chloroform (50 c.c.), and phosphorus pentachloride (6 g.) was allowed to remain at room temperature for 36 hours. The solvent was removed in a vacuum from the buff-coloured solid, the residue was dissolved in hot water, and the filtered solution made alkaline with ammonia. The solid base, collected after 3 hours, crystallised from ethyl alcohol in pale yellow prisms (3·9 g.), m. p. 159—160° (Found: C, 61·9; H, 5·9. $C_{20}H_{22}O_6N_2$ requires C, 62·2; H, 5·7%). This *base* is almost insoluble in light petroleum, sparingly soluble in ether and cold alcohol, but readily soluble in benzene and chloroform. It dissolves in hot dilute hydrochloric acid, and on cooling, the *hydrochloride* separates in very pale yellow needles, m. p. 227° (decomp.). The *methiodide* was prepared by allowing the base to react with an excess of methyl iodide at room temperature for 12 hours. The excess of methyl iodide was then removed, and the residue crystallised from ethyl alcohol, in which it was readily soluble. It forms rosettes of yellow needles, which contain solvent of crystallisation and melt at 105—107°, resolidify, and decompose gradually between 180° and 190° (Found in material dried at 100°: C, 47·7; H, 5·0. $C_{21}H_{25}O_6N_2I$ requires C, 47·7; H, 4·7%).

*2'-Amino-6 : 7 : 3' : 4'-tetramethoxy-1-benzyl-2-methyltetrahydroiso*quinoline (III).—A hot solution of the methiodide (2·3 g.) in water (25 c.c.) and concentrated hydrochloric acid (25 c.c.) was reduced by the gradual addition of zinc dust (7·5 g.). The liquid having been filtered and made alkaline with ammonia, the base was extracted with ether and dried, and the solvent removed. The residual oil was dissolved in chloroform and saturated with dry hydrogen chloride; the *dihydrochloride* of the base (III) separated in colourless needles (1·7 g.), m. p. 188—190° (Found in material dried at 100°: C, 56·8; H, 6·7. $C_{21}H_{28}O_4N_2$,2HCl requires C, 56·6; H, 6·7%). The dihydrochloride was hygroscopic and dissolved readily in ethyl alcohol. The addition of sodium nitrite to an aqueous solution of the dihydrochloride produced a bright yellow solution which coupled with alkaline β-naphthol, yielding a vermilion azo-dye which became deep port-wine in colour when dissolved in concentrated sulphuric acid.

dl-*Corytuberine dimethyl ether* (IV).—The dihydrochloride of the base (III) (2 g.), dissolved in methyl alcohol (10 c.c.) and sulphuric acid (10 c.c. of 2*N*), was diazotised by the gradual addition of the calculated amount of 2*N*-sodium nitrite. The bright yellow liquid became deep red after boiling for ½ hour; zinc dust (1 g.) and con-

centrated hydrochloric acid (3 c.c.) were then added, and the boiling was continued for 15 minutes. The mixture was filtered, and the residue extracted with boiling water. The combined filtrate and washings were rendered alkaline with ammonia and extracted with ether, the extract was washed with sodium hydroxide solution and dried, and the ether was removed. *dl*-Corytuberine dimethyl ether (0·3 g.) remained as a pale yellow oil which did not crystallise. The *hydrochloride* was very soluble in water and alcohol, and the *hydriodide* separated as a gum when potassium iodide was added to an aqueous solution of the hydrochloride. The *methiodide*, which was obtained by heating the *dl*-base with an excess of methyl iodide, crystallised from ethyl alcohol in colourless prisms which darken slightly at about 220° and decompose at 248° (Found: C, 52·9; H, 5·5. $C_{22}H_{28}O_4NI$ requires C, 53·1; H, 5·6%).

Resolution of dl-*Corytuberine Dimethyl Ether.*—When *dl*-corytuberine dimethyl ether (1 g.) in absolute ethyl alcohol (15 c.c.) was mixed with an absolute-ethyl-alcoholic solution of *d*-tartaric acid (3 c.c. of 2*N*), a gum separated. This dissolved on boiling, and the colourless crystals of l-*corytuberine dimethyl ether* d-*bitartrate* which rapidly separated were collected by filtering the boiling solution and recrystallised from rectified spirit, forming colourless needles, m. p. 219—221° (decomp.) (Found in material dried at 100°: C, 59·2; H, 6·3. $C_{25}H_{31}O_{10}N$ requires C, 59·4; H, 6·1%). In aqueous solution: $l = 1$, $c = 1{\cdot}005$, $\alpha_D = -1{\cdot}49°$, whence $[\alpha]_D = -148{\cdot}2°$. On cooling, the hot filtrate deposited a gum; the clear supernatant liquid was decanted and evaporated to dryness and the base was liberated by the action of sodium hydroxide solution and extracted with ether. The ethereal extract was dried, the solvent removed, and the residual oil was dissolved in absolute ethyl alcohol (15 c.c.) and mixed with an absolute-ethyl-alcoholic solution of *l*-tartaric acid (3 c.c. of 2*N*). *d*-Corytuberine dimethyl ether *l*-bitartrate separated; it crystallised from rectified spirit in colourless needles, m. p. 219—222° (decomp.). Gadamer (*loc. cit.*) gives 219—224° (decomp.) (Found: C, 59·3; H, 6·3. Calc. for $C_{25}H_{31}O_{10}N$: C, 59·4; H, 6·1%). In aqueous solution, $l = 1$, $c = 1{\cdot}017$, $\alpha_D = +1{\cdot}53°$, whence $[\alpha]_D = +149{\cdot}7°$. Gadamer (*loc. cit.*) gives $[\alpha]_D = +150°$.

The *d*- and the *l*-base were liberated as oils from the bitartrates by the action of sodium hydroxide solution. With concentrated sulphuric acid, concentrated nitric acid, Erdmann's reagent, Fröhde's reagent, Mandelin's reagent, and a solution of selenic acid in concentrated sulphuric acid, the *d*- or the *l*-base gave colour reactions which were in agreement with those described by Gadamer (*loc. cit.*) for *d*-corytuberine dimethyl ether.

d-Corytuberine dimethyl ether *methochloride* was prepared by refluxing the *d*-base with an excess of methyl iodide for 1 hour, removing the excess of methyl iodide, digesting the residual methiodide with an aqueous suspension of silver chloride for 2 hours, filtering the solution, and evaporating the filtrate to dryness. When ether was added gradually to a solution of the gummy residue in a little absolute ethyl alcohol, the methochloride separated in slender needles, m. p. 243° (decomp.). Gadamer gives m. p. 234—237° (decomp.). In aqneous solution: $l = 1$, $c = 1{\cdot}112$, $\alpha_D = +2{\cdot}17°$, whence $[\alpha]_D = +196°$. Gadamer gives 197·6°.

Carbethoxycorytuberine dimethyl ether (V), m. p. 93°, was prepared from the synthetical *d*- or *dl*-base by the process described by Osada (*loc. cit.*) and appeared to be identical with that obtained from natural sources.

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CCXXXVIII.—*Syntheses in the Diphenyl Series.*

By LEONARD ERIC HINKEL and DONALD HOLROYDE HEY.

THE view (this vol., p. 1200) that 4 : 5 : 5-tribromo-1-phenyl*cyclo*hexan-3-one, when heated alone or with alcoholic potassium hydroxide, decomposes into 5-bromo-3-hydroxydiphenyl and 4 : 5-dibromo-3-hydroxydiphenyl has now been shown to be correct. The constitutions of the two compounds have been proved by their syntheses from 5-bromo-3-nitro-4-aminodiphenyl through 5-bromo-3-nitrodiphenyl and 5-*bromo*-3-*aminodiphenyl* in the first case, and through 4 : 5-*dibromo*-3-*nitrodiphenyl* and 4 : 5-*dibromo*-3-*aminodiphenyl* in the second.

No trace of 4 : 5-dibromo-3-nitrodiphenyl was obtained from 5-bromo-3-nitro-4-aminodiphenyl by diazotisation in hydrobromic acid solution as described by Crossley (J., 1904, **85**, 278): the amino-group appeared to be unaffected, but the bromine formed by the interaction of the nitrous and hydrobromic acids reacted readily with the base, giving rise to 5 : 4′-dibromo-3-nitro-4-aminodiphenyl. This formed golden-orange needles, m. p. 154°. Scarborough and Waters (J., 1927, 1138), who obtained this compound by the bromination of 5-bromo-3-nitro-4-aminodiphenyl, describe it as red needles, m. p. 158°. We have repeated their experiment,

carrying out the heating process for only 2 hours, and obtained the dibromo-derivative as golden-orange needles, m. p. 154°; longer heating, as carried out by them, not only diminished the yield but also produced small quantities of darker-coloured substances. Acetylation of the dibromo-compound gave a product, m. p. 153°, which was identical with a specimen kindly provided by Bell and Robinson, who prepared it by the bromination of 3-nitro-4-acetamidodiphenyl (J., 1927, 1130). Reduction of the base gave 5 : 4′-*dibromo*-3 : 4-*diaminodiphenyl.*

EXPERIMENTAL.

5-Bromo-3-nitro-4-aminodiphenyl.—3-Nitro-4-aminodiphenyl was brominated as described by Scarborough and Waters (*loc. cit.*). By slow crystallisation from methyl alcohol the product was obtained pure as deep orange needles, m. p. 100° (Found : Br, 27·2. Calc. : Br, 27·3%).

Acetylation of the base gave 5-bromo-3-nitro-4-acetamidodiphenyl, which crystallised from alcohol in orange-yellow needles m. p. 95°, and was identical with the compound described by Bell and Robinson (*loc. cit.*) as (5 ?)-bromo-3-nitro-4-acetamidodiphenyl, m. p. 94—95°.

5-Bromo-3-aminodiphenyl.—5-Bromo-3-nitrodiphenyl (Scarborough and Waters, *loc. cit.*) was reduced in alcoholic solution with sodium hydrosulphite. After removal of the alcohol under reduced pressure, the *base* was extracted with ether. It crystallised from light petroleum (b. p. 40—60°) in light brown prisms, m. p. 88° (Found : Br, 32·1. $C_{12}H_{10}NBr$ requires Br, 32·3%).

The *acetyl* derivative, prepared in the usual manner, crystallised from alcohol–light petroleum in white prisms, m. p. 140° (Found : Br, 26·9. $C_{14}H_{12}ONBr$ requires Br, 27·6%).

5-Bromo-3-benzoyloxydiphenyl.—5-Bromo-3-aminodiphenyl was diazotised in the usual manner in an 80% solution of sulphuric acid at 0°. After remaining for 1 hour at this temperature, the solution was gradually heated to boiling, then diluted, and extracted with ether. The dark oil remaining after removal of the ether was treated with sodium hydroxide solution. Acidification of the alkaline solution precipitated 5-bromo-3-hydroxydiphenyl as an oil which owing to the small amount available was not further purified but converted directly into its benzoyl derivative; this crystallised from alcohol in clusters of small needles, m. p. 108°, unchanged by admixture with the benzoyl derivative of 5-bromo-3-hydroxydiphenyl (this vol., p. 1203).

4 : *5-Dibromo-3-nitrodiphenyl.*—4 G. of 5-bromo-3-nitro-4-aminodiphenyl were diazotised as described above. The solution was

diluted with ice-water, poured into a cold solution of cuprous bromide in hydrobromic acid, and gradually heated to boiling. Extraction of the solution with ether gave a solid which crystallised from methyl alcohol in pale yellow needles, m. p. 125° (Found: Br, 44·6. $C_{12}H_7O_2NBr_2$ requires Br, 44·8%). Oxidation with chromic acid in glacial acetic acid solution gave 4 : 5-dibromo-3-nitrobenzoic acid (m. p. 182°).

4 : 5-*Dibromo-3-acetamidodiphenyl*.—4 : 5-Dibromo-3-nitrodiphenyl was reduced with sodium hydrosulphite, and the brown semi-solid base obtained was converted by the usual method into the *acetyl derivative*, which crystallised from aqueous alcohol in white needles, m. p. 177° (Found: Br, 43·5. $C_{14}H_{11}ONBr_2$ requires Br, 43·4%).

On hydrolysis of the acetyl derivative with concentrated hydrochloric acid and subsequent treatment with ammonia, the base was obtained as a dark semi-solid mass, which was converted into 4 : 5-dibromo-3-hydroxydiphenyl by the diazo-reaction. This crystallised from light petroleum (b. p. 40—60°) in fine needles, m. p. 81°, and its benzoyl derivative, prepared in the usual manner, crystallised from alcohol in small, white needles, m. p. 104°. These m. p.'s were unchanged by admixture with the corresponding compounds described in this vol., p. 1203.

5 : 4'-*Dibromo-3 : 4-diaminodiphenyl*, obtained by reducing 5 : 4'-dibromo-3-nitro-4-aminodiphenyl with sodium hydrosulphite, crystallised from alcohol in white needles, m. p. 120° (Found: Br, 46·9. $C_{12}H_{10}N_2Br_2$ requires Br, 46·8%). The *dibenzoyl* derivative, prepared in the usual manner, was sparingly soluble in boiling alcohol, from which it separated in microscopic crystals, m. p. 278° (Found: Br, 29·2. $C_{26}H_{18}O_2N_2Br_2$ requires Br, 29·1%).

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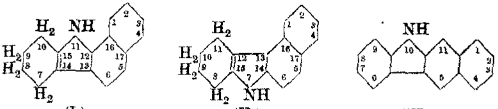
CCXXXIX.—*Derivatives of 7 : 8 : 9 : 10-Tetrahydro-αβ-naphthacarbazole and of 8 : 9 : 10 : 11-Tetrahydro-α'β'-naphthacarbazole.*

By STEPHEN HELLICAR OAKESHOTT and SYDNEY GLENN PRESTON PLANT.

THE reactions observed with tetrahydrocarbazole and its 9-acyl derivatives, especially those with nitric acid which involve the addition of OH and NO_2 or OH and OH to the double linkage (Perkin and Plant, J., 1921, **119**, 1825; 1923, **123**, 676), made it probable that the investigation of 7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole (1) and 8 : 9 : 10 : 11-tetrahydro-α'β'-naphtha-

carbazole (II) along similar lines would present many interesting points.



(I.) (II.) (III.)

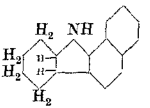
These two compounds (named $\Delta^{1(6)}$-tetrahydrobenzo-α- and -β-naphthindole) have already been prepared by Borsche, Witte, and Bothe (*Annalen*, 1908, **359**, 64) from *cyclo*hexanone-α- and -β-naphthylhydrazone respectively, and these authors have established the constitution of (I) by oxidising it to αβ-naphthacarbazole with lead oxide. There could be no reasonable doubt concerning the structure of (II), but it has now been confirmed by dehydrogenation with sulphur to α′β′-naphthacarbazole, thus disposing of the alternative ββ-naphthacarbazole skeleton (III).

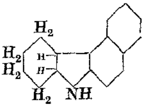
Attempts to acetylate 7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole directly with acetic anhydride failed, but the action of acetyl chloride on magnesium 11-7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazyl bromide yielded *11-acetyl-7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole*. The *11-benzoyl* compound was similarly obtained. An investigation of the action of nitric acid on 7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole and its acetyl and benzoyl derivatives has yielded no crystalline substance, with the exception of a *trinitro*-derivative from the benzoyl compound.

The action of hot acetic anhydride on 8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole in the presence of a few drops of concentrated sulphuric acid gives first *7-acetyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole*, but a *diacetyl* derivative is soon formed in which one of the acetyl groups must be attached to carbon and the other to nitrogen. On boiling with aqueous-alcoholic potassium hydroxide, the acetyl group attached to nitrogen is removed with the production of *C-monoacetyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole*, the nature of which is confirmed by the fact that it gives an *oxime*. The point of attachment of the *C*-acetyl group has not been determined. *7-Acetyl-* and *7-benzoyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole* can be most conveniently obtained by means of the Grignard reaction in processes similar to those used for the isomeric derivatives of αβ-naphthacarbazole. From the product of the action of nitric acid in glacial acetic acid solution on each of these acyl derivatives of (II), a *mononitro*-derivative has been isolated, but from none of the acyl derivatives studied in the naphthacarbazole

series have products formed by the addition of OH and NO_2 or OH and OH to the double linkage been isolated. It is not possible to state definitely that such reactions do not occur, since in many experiments a considerable portion of the product could not be crystallised nor its nature determined.

Compounds (I) and (II) have been reduced to *7 : 8 : 9 : 10 : 14 : 15-hexahydro-αβ-naphthacarbazole* (IV) and *8 : 9 : 10 : 11 : 12 : 15-hexahydro-α'β'-naphthacarbazole* (V) respectively. Theoretically

(IV.) 

 (V.)

each of these hexahydro-derivatives should exist in two stereoisomeric forms (*cis*- and *trans*-) analogous to the two forms of hexahydrocarbazole (Gurney, Perkin, and Plant, J., 1927, 2676), but the formation of the *trans*-modification in other than very small quantities in each case is not to be expected on account of the much greater strain in these configurations. Therefore the two hexahydronaphthacarbazoles here described almost certainly have the *cis*-configurations (IV and V). The former can be prepared by the electrolytic reduction of the corresponding tetrahydro-compound, but a similar method for (V) gave a very poor yield, hydriodic acid and phosphorus being used finally for the reduction.

EXPERIMENTAL.

7 : 8 : 9 : 10-Tetrahydro-αβ-naphthacarbazole (I).—α-Naphthylhydrazine hydrochloride, prepared from α-naphthylamine (100 g.) by the method of Fischer (*Annalen*, 1886, **232**, 236), was mixed with alcohol (1000 c.c.) and shaken for a short time at 50—60° with crystallised sodium acetate (80 g.); *cyclo*hexanone (60 c.c.) was then added and, after ½ hour, the solution was diluted with water (2000 c.c.). The hydrazone separated as a sticky mass which was washed with water and warmed with 1100 c.c. of 14% sulphuric acid (by vol.); the compound (I) then separated in good yield. It was recrystallised from glacial acetic acid and obtained in colourless needles, m. p. 139—140° (compare Borsche, Witte, and Bothe, *loc. cit.*). It can also be obtained by boiling the alcoholic mixture of crude α-naphthylhydrazine hydrochloride, sodium acetate, and *cyclo*hexanone. The product soon begins to separate, and can be isolated in a pure condition by adding an equal volume of water and cooling the mixture. Its *picrate* separates from benzene in very dark brown prisms, m. p. 172° (decomp.). All attempts to

nitrate the compound (I) in either acetic acid or sulphuric acid solution failed to yield any crystalline substance.

Oxidation of 7 : 8 : 9 : 10-*Tetrahydro-αβ-naphthacarbazole*.—A mixture of this compound (6·8 g.), sulphur (2 g.), and quinoline (20 c.c.) was boiled for 45 minutes, cooled, and poured into a mixture of ice and dilute hydrochloric acid. The sticky product was washed with dilute hydrochloric acid, dried, mixed with a little iron filings, and distilled. The αβ-naphthacarbazole obtained crystallised from benzene–petroleum in colourless needles, m. p. 225—226°. It dissolved in concentrated sulphuric acid to give a yellow solution, which changed to a dark green on the addition of a drop of concentrated nitric acid. There is no doubt that this product is identical with the αβ-naphthacarbazole previously described (compare, *e.g.*, Japp and Maitland, J., 1903, **83**, 267: Borsche, Witte, and Bothe, *loc. cit.*; Bucherer and Schmidt, *J. pr. Chem.*, 1909, **79**, 384).

11-*Acetyl*-7 : 8 : 9 : 10-*tetrahydro-αβ-naphthacarbazole*.—Magnesium (4·8 g.) was dissolved in a mixture of ethyl bromide (16 c.c.) and ether (150 c.c.). When a solution of the compound (I) (25 g.) in dry ether was slowly added, a brisk evolution of ethane occurred and a dark oil separated. The mixture was treated gradually with acetyl chloride (15 c.c.), warmed on the water-bath for a few minutes, and then cautiously treated with ice and dilute hydrochloric acid. The whole was extracted with more ether, and the extract was washed with aqueous sodium carbonate and dried over potassium carbonate. After removal of the solvent, the residue was crystallised from glacial acetic acid or methyl alcohol, from which 11-*acetyl*-7 : 8 : 9 : 10-*tetrahydro-αβ-naphthacarbazole* separated in colourless needles, m. p. 125° (Found: N, 5·2. $C_{18}H_{17}ON$ requires N, 5·3%). This acetyl derivative is slightly soluble in cold ether and alcohol, readily soluble in benzene, and practically insoluble in petroleum.

11-*Benzoyl*-7 : 8 : 9 : 10-*tetrahydro-αβ-naphthacarbazole* was prepared similarly, benzoyl chloride being used in place of acetyl chloride. The crude product was a dark yellow syrup, which crystallised on treatment with glacial acetic acid, and after recrystallisation from petroleum (b. p. 100—120°) 11-*benzoyl*-7 : 8 : 9 : 10-*tetrahydro-αβ-naphthacarbazole* separated in short, yellow needles, m. p. 146—147° (Found: N, 4·3. $C_{23}H_{19}ON$ requires N, 4·3%).

When a solution of the benzoyl derivative (1 g.) in glacial acetic acid (10 c.c.) at 95° was treated with nitric acid (5 c.c. of *d* 1·4), left at 100° for ½ hour, and then kept over-night, *trinitro*-11-*benzoyl*-7 : 8 : 9 : 10-*tetrahydro-αβ-naphthacarbazole* separated; after recrystallisation from acetone, it was obtained in yellow needles, m. p. 255° (decomp.) (Found: C, 60·8; H, 3·3; N, 12·2. $C_{23}H_{16}O_7N_4$

requires C, 60·0; H, 3·5; N, 12·2%). Attempts to control this reaction in order to isolate simpler products yielded no crystalline material.

7 : 8 : 9 : 10 : 14 : 15-*Hexahydro*-αβ-*naphthacarbazole*.—A solution of the compound (I) (10 g.) in a mixture of sulphuric acid (100 c.c. of *d* 1·5) and alcohol (100 c.c.) at 80° was submitted to electrolytic reduction during 20 hours, lead electrodes and a current of 5 amps. (0·03 amp. per sq. cm. of cathode) being used. The mixture was diluted with water (300 c.c.), filtered, and made alkaline with concentrated aqueous ammonia. Ether extracted an oil which solidified when left in contact with petroleum. On recrystallisation from a small quantity of methyl alcohol, 7 : 8 : 9 : 10 : 14 : 15-*hexahydro*-αβ-*naphthacarbazole* was obtained in colourless needles, m. p. 88° (Found: C, 86·2; H, 7·7. $C_{16}H_{17}N$ requires C, 86·1; H, 7·6%). The base soon develops a mauve colour on exposure to the air, is readily soluble in ether with a blue fluorescence, and gives with mineral acids salts which are only slightly soluble in water.

A solution of the base (2·2 g.) in glacial acetic acid (7 c.c.), after being treated with concentrated nitric acid (2 c.c., previously treated with urea nitrate) dissolved in acetic acid (3 c.c.), was diluted with water (10 c.c), and made alkaline with ammonia. Ether extracted a syrup which was crystallised from alcohol, *dinitro*-7 : 8 : 9 : 10 : 14 : 15-*hexahydro*-αβ-*naphthacarbazole* separating in small, yellow needles, m. p. 139—140° (Found: N, 13·6. $C_{16}H_{15}O_4N_3$ requires N, 13·4%).

11-*Acetyl*-7 : 8 : 9 : 10 : 14 : 15-*hexahydro*-αβ-*naphthacarbazole*.—A mixture of 7 : 8 : 9 : 10 : 14 : 15-hexahydro-αβ-naphthacarbazole (2 g.) and acetic anhydride (10 c.c.) was boiled for 5 minutes, allowed to cool, diluted with water, and left over-night. The product crystallised from a small quantity of petroleum (b. p. 80—100°) in long, colourless needles, m. p. 132° (Found: N, 5·3. $C_{18}H_{19}ON$ requires N, 5·3%).

11-*Benzoyl*-7 : 8 : 9 : 10 : 14 : 15-*hexahydro*-αβ-*naphthacarbazole*.—The base (5 g.) was shaken with aqueous sodium hydroxide and benzoyl chloride (6 g.). The product separated as a crystalline mass and after recrystallisation from methyl alcohol was obtained in colourless needles, m. p. 148—149° (Found: N, 4·3. $C_{23}H_{21}ON$ requires N, 4·3%).

8 : 9 : 10 : 11-*Tetrahydro*-α′β′-*naphthacarbazole* (II).—This substance was obtained by a process similar to that described for compound (I) but using β-naphthylhydrazine hydrochloride. It separated from glacial acetic acid in colourless prisms, m. p. 137° (Found: C, 86·9; H, 7·0. Calc.: C, 86·9; H, 6·8%). Borsche, Witte, and Bothe (*loc. cit.*) give the m. p. 152°. When equal

quantities of the compound (II) and picric acid were mixed in hot alcohol, the solution filtered and allowed to cool, the *picrate* separated in black needles, m. p. 194° (decomp.). Attempts to nitrate the compound (II) yielded nothing crystalline.

Oxidation of 8 : 9 : 10 : 11-*Tetrahydro*-α′β′-*naphthacarbazole*.—This was carried out as described on p. 1843. The semi-solid distillate was dissolved in toluene and the solution was dried over calcium chloride, filtered, and treated with a toluene solution of picric acid. The crimson picrate, m. p. 165—168°, which separated was decomposed by grinding with dilute aqueous sodium hydroxide, and the product was dried and recrystallised from benzene–petroleum; α′β′-naphthacarbazole then separated in colourless plates, m. p. 134—135° (Found: C, 88·7; H, 5·1. Calc.: C, 88·5; H, 5·1%). The mixture with compound (II) melted completely below 110°. α′β′-Naphthacarbazole, prepared in this way, dissolved in concentrated sulphuric acid to give a yellowish-brown solution which turned yellowish-green on addition of a drop of concentrated nitric acid (compare Ullmann, *Annalen*, 1904, **332**, 102), and gave a picrate which separated from toluene in crimson plates, m. p. 175° (compare Japp and Maitland, *loc. cit.*). There can be no doubt, therefore, that this product is identical with the α′β′-naphthacarbazole previously described. The isomeric ββ′-naphthacarbazole melts at 330° (Graebe and Knecht, *Annalen*, 1880, **202**, 1).

Acetyl Derivatives of 8 : 9 : 10 : 11-*Tetrahydro*-α′β′-*naphthacarbazole*.—Boiling acetic anhydride alone has no action on the compound (II). When, however, the substance (10 g.) was boiled for 45 minutes with acetic anhydride (60 c.c.) containing a few drops of concentrated sulphuric acid, a dark green solid separated. After recrystallisation from glacial acetic acid containing some charcoal, a C-*acetyl*-7-*acetyl*-8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazole* separated in greenish-yellow prisms, m. p. 185° (Found: C, 78·8; H, 6·2; N, 4·7. $C_{20}H_{19}O_2N$ requires C, 78·7; H, 6·2; N, 4·6%). This diacetyl derivative (4 g.) was heated on the water-bath for ½ hour with potassium hydroxide (8 g.) dissolved in aqueous alcohol, the alcohol distilled off, and the residue treated with water; C-*acetyl*-8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazole* then remained and after crystallisation from alcohol was obtained in yellow plates, m. p. 213° (Found: N, 5·2. $C_{18}H_{17}ON$ requires N, 5·3%). This regenerated the diacetyl compound (m. p. 185°) when treated with acetic anhydride and a drop of concentrated sulphuric acid on the water-bath, and when boiled for an hour with an excess of hydroxylamine hydrochloride and sodium acetate in alcohol, yielded an *oxime* which crystallised from aqueous alcohol in pale yellow plates, m. p. 213—216° (Found: N, 10·2. $C_{18}H_{18}ON_2$ requires N, 10·1%).

When the compound (II) was warmed on the water-bath with acetic anhydride containing a few drops of concentrated sulphuric acid for 5 minutes only and the mixture cooled and diluted with water, the product, after crystallisation from alcohol and then from glacial acetic acid, yielded *7-acetyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole* in colourless plates, m. p. 162° (Found: N, 5·2. $C_{18}H_{17}ON$ requires N, 5·3%). Owing to the readiness with which the diacetyl derivative (m. p. 185°) is produced, it is, however, difficult to prepare 7-acetyl-8 : 9 : 10 : 11-tetrahyro-α′β′-naphthacarbazole in any quantity by this method, and a much more satisfactory process is to use the Grignard reagent as described above for the preparation of 11-acetyl-7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole. In this case the product was practically insoluble in either the ether or the aqueous layer, and was collected by filtration and recrystallised from glacial acetic acid. 7-Acetyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole was hydrolysed to the compound (II) on boiling its alcoholic solution with potassium hydroxide for ½ hour, the product being obtained on diluting the solution with water.

7-Acetyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole (5 g.), dissolved in glacial acetic acid (50 c.c.) at 95°, was treated gradually with nitric acid (2 c.c. of *d* 1·4) in a little acetic acid. Almost immediately a yellow product (2·5 g.), melting indefinitely at about 190°, separated. It was collected after a few hours and crystallised from toluene and then from *cyclo*hexanone. After further recrystallisation from *cyclo*hexanone a *mononitro-7-acetyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole* was obtained in bright yellow needles, m. p. 222° (Found: N, 9·0. $C_{18}H_{16}O_3N_2$ requires N, 9·1%). It was evident that this is not the only product of this reaction, but efforts to isolate any other substance in a pure condition have so far been unsuccessful.

7-Benzoyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole.—This derivative was obtained by a process similar to that described for the corresponding 11-benzoyl-7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole. After crystallisation from glacial acetic acid, it separated in clusters of yellowish prisms, m. p. 139° (Found: N, 4·3. $C_{23}H_{19}ON$ requires N, 4·3%).

7-Benzoyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole (2 g.) was dissolved in glacial acetic acid (40 c.c.) at 80° and treated with nitric acid (1·5 c.c. of *d* 1·5) in a little glacial acetic acid. The mixture was cooled and kept for some days and the product was then collected and crystallised from acetone, from which *mononitro-7-benzoyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole* separated in yellow needles, m. p. 208—209° (Found: C, 74·8; H, 5·1. $C_{23}H_{18}O_3N_2$ requires C, 74·6; H, 4·9%).

8 : 9 : 10 : 11 : 12 : 15-*Hexahydro-α′β′-naphthacarbazole*.—A mixture of the compound (II) (10 g.), red phosphorus (7 g.), and hydriodic acid (70 c.c. of *d* 1·9) was boiled for 18 hours, cooled, made alkaline with aqueous sodium hydroxide, and extracted with ether. The extract was washed with water and dried over potassium carbonate and then dry hydrogen chloride was passed into it. 8 : 9 : 10 : 11 : 12 : 15-*Hexahydro-α′β′-naphthacarbazole hydrochloride* separated; after recrystallisation from hot water, it was obtained in small, buff-coloured prisms, m. p. 265° with sublimation (Found: C, 73·7; H, 7·0. $C_{16}H_{17}N,HCl$ requires C, 73·9; H, 6·9%). The base, liberated by treating the hydrochloride with aqueous sodium hydroxide and isolated by means of ether, was obtained only as a syrup, b. p. 198—202°/10 mm.

7-*Acetyl*-8 : 9 : 10 : 11 : 12 : 15-*hexahydro*-α′β′-*naphthacarbazole* was obtained by boiling the base with acetic anhydride for 5 minutes and then diluting the solution with water. It separated from dilute alcohol in colourless plates, m. p. 120° (Found: N, 5·2. $C_{18}H_{19}ON$ requires N, 5·3%).

7-*Benzoyl*-8 : 9 : 10 : 11 : 12 : 15-*hexahydro-α′β′-naphthacarbazole*.—A mixture of the base (2 g.) and benzoic anhydride (2·4 g.) was heated at 150°, cooled, dissolved in chloroform, washed with aqueous sodium carbonate, and dried over potassium carbonate; the solvent was then removed and on crystallisation from petroleum (b. p. 60—80°) the product was obtained in colourless prisms, m. p. 131° (Found: N, 4·3. $C_{23}H_{21}ON$ requires N, 4·3%).

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CCXL.—*The Preparation and Properties of Pure Phosphorus Trioxide.*

By CHRISTINA CRUICKSHANK MILLER.

THE luminescence exhibited by slowly oxidising phosphorus trioxide has been frequently commented on and studied since the preparation of the oxide by Thorpe and Tutton (J., 1890, **57**, 545) and their study of its properties. Many have been the attempts to find the relation between the glowing of phosphorus and the glowing of its oxide. Although the best conditions for production of the glow in the two cases are by no means the same, there are several striking

points of resemblance: for example, Emeléus (*J.*, 1925, **127**, 1362) established the identity of the ultra-violet band spectra, and Downey (*ibid.*, 1924, **125**, 347) showed that the light from each is capable of ionising oxygen; also Scharff (*Z. physikal. Chem.*, 1908, **62**, 179) found that substances which inhibit the glow of phosphorus likewise inhibit that of the trioxide.

The possibility of the glow being due to phosphorus in the oxide was considered by Thorpe and Tutton but rejected as unlikely. It is now shown, however, that Thorpe and Tutton did not study an oxide free from phosphorus, and that many properties supposed to be characteristic of phosphorus trioxide may, indeed, be due to dissolved phosphorus.

In an earlier paper (Miller, *Proc. Roy. Soc. Edin.*, 1926, **46**, 76) it was shown that there was a connexion between the glowing of phosphorus trioxide and the presence of water vapour. The effect on phosphorus trioxide, in evacuated bulbs, of water vapour derived from certain salt–hydrate mixtures was such as to indicate the possibility of formation of hydrides of phosphorus. It has since been found, however, that the use of hydrated chlorides and sulphates leads to erroneous results owing to the liberation of hydrogen chloride from chlorides and of sulphur dioxide from sulphates. When chlorides are used, gaseous hydrogen phosphide has been definitely proved to be amongst the final products, but its formation is due to complicated reactions which ensue between the hydrochloric acid and the phosphorus trioxide, not to direct action of aqueous vapour on the trioxide. When sulphates are used no hydrogen phosphide is produced. The very slight increase of pressure observed when water itself was the source of moisture is now attributed to carbon dioxide initially dissolved in the oxide and liberated in part by the conversion of phosphorus trioxide into phosphorous acid. In subsequent experiments water vapour at various pressures was obtained by the use of aqueous solutions of orthophosphoric acid, which produced no pressure change in presence of phosphorus trioxide in evacuated bulbs.

The Rate of Oxidation of Phosphorus Trioxide.

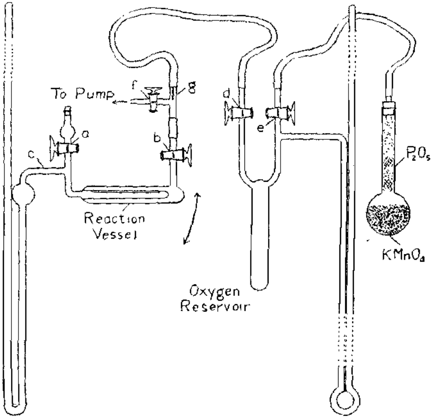
The rate of oxidation in oxygen, at 25°, of phosphorus trioxide, prepared according to Thorpe and Tutton's method and distilled at low pressure over reduced copper gauze, was studied in presence of the following solutions of phosphoric acid:

H_3PO_4 (g. per 100 g. of solution) ...	50	80	90	97
Density at 25°	1·335	1·629	1·743	1·845
Aqueous tension at 25° (mm.)	16·7	4·0	1·2	0·2

(If moisture was excluded from the apparatus oxygen was absorbed at an extremely slow rate.)

The apparatus (*shown to the left* in Fig. 1) was a slight modification of that used with hydrate mixtures (*loc. cit.*) and consisted of a bulb into one end of which was sealed a glass boat. Phosphorus trioxide was run into the boat at *a* and phosphoric acid into the wide tube at *b*. On to the apparatus was sealed a mercury manometer, and the whole was held pivoted at *c* so that an up and down movement could be effected as shown by the arrow. The volume of the bulb was a minimum, 30 c.c., so as to maintain the saturated vapour pressure of phosphorus trioxide, and the shaking device prevented film formation on the liquids.

FIG. 1.

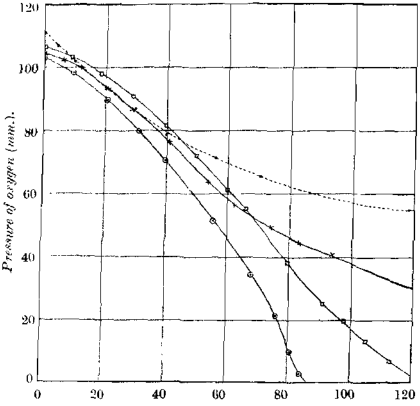


In all experiments the same quantities of liquids were used, *viz.*, 1·2 c.c. of phosphorus trioxide and 8 c.c. of a phosphoric acid solution, a choice which did not introduce a marked change in the pressure of water vapour as the oxide was used up. The apparatus containing phosphoric acid was evacuated, and oxygen, generated by heating potassium permanganate, passed in till its partial pressure was 00—110 mm. After the apparatus had been heated to 25°, liquid phosphorus trioxide was run into the boat and pressure readings were made at intervals. The pressure–time curves (Fig. 2) illustrate he nature of the results.

Experiment 1. When the pressure of water vapour was very

low—0·2 mm.—oxygen was absorbed at a slowly increasing rate until all had gone in 1½ hours. During oxidation, glowing and flashing took place in the vapour phase, the luminescence always tending to be away from the phosphorus trioxide source, *i.e.*, not above the boat. *Luminescence was all the time of the same nature*, but brighter at lower pressures, and it faded and disappeared abruptly when nearly all the oxygen was used up. Most of the phosphorus trioxide seemed to be oxidised.

FIG. 2.



⊙ *Pressure of water vapour* 0·2 *mm.*; □ 1·2 *mm.*;
× 4·0 *mm.*; • 16·7 *mm.*

Experiment 2. The rate of absorption of oxygen in presence of 1·2 mm. pressure of water vapour was similar to that in Expt. 1, but the rate fell off after about 70 minutes. The glow phenomena up to this point were also similar, except that glowing took place to a slight extent above the boat. After 90 minutes, when the rate of oxidation was slower, there was permanent glowing round numerous solid particles in the boat. This was not observed when the pressure of water vapour was very low. No phosphorus trioxide remained.

Experiment 3. When the pressure of water vapour was 4 mm the rate of oxidation for 40 minutes was similar to that in the two

preceding experiments. The glow tended very early to pass above the boat, and steady glowing showed at numerous points in the boat, earlier than in Expt. 2. The passing of the glow to the boat coincided with a reduction in the rate of absorption of oxygen and with the disappearance of phosphorus trioxide.

Experiment 4. With a high pressure of water vapour, flashing occurred after a few minutes above the boat, and in 10 minutes steady glowing took place in the boat. The phosphorus trioxide was practically all used up. After ½ hour the only glowing was that round the solid particles in the boat, and the fairly rapid initial rate of oxygen absorption had given way to a very slow absorption.

In these experiments it was found that the bulk of the phosphorus trioxide was converted into phosphorous acid, which did not absorb oxygen under the conditions prevailing. When the pressure of water vapour was high, this conversion was very rapid, and the subsequent slow rate of oxygen absorption was therefore not due to phosphorus trioxide. In all experiments, after the oxygen was used up, a small, insoluble residue, consisting of minute particles surrounded by liquid, remained in the boat; this was apparently phosphorus, for it glowed in air. The glowing previously observed in the boat was around these particles. As a test, 40 mg. of phosphorus were disintegrated in 2 c.c. of a 50% solution of phosphoric acid and part of the mixture was oxidised as in Expts. 1—4. Glowing took place round the solid particles and the pressure fell at a measurable rate, depending on the quantity of mixture present and on the amount of liquid surrounding the particles. The appearance of phosphorus in the boat in Expts. 1—4 was attributed to phosphorus originally dissolved in the phosphorus trioxide and set free by the conversion of the oxide into phosphorous acid. As the phosphorus trioxide might contain 1% of phosphorus, as judged by results of analysis, its rate of oxidation was compared with that of a 1% solution of phosphorus in paraffin oil. With the latter the pressure of oxygen fell 100 mm. in 3—4 minutes. This rapid rate of oxidation therefore bore no resemblance to the rates found for phosphorus trioxide. Glowing appeared only at the surface of the paraffin solution.

The rate of oxygen absorption by phosphorus trioxide, with low water-vapour pressure, was examined at constant pressure and volume. The boat tube was connected as shown in Fig. 1 with a 5—55 c.c. oxygen reservoir, to which were attached a mercury manometer, reading up to 800 mm. pressure, and a flask in which oxygen was generated by heating potassium permanganate, and dried by passage through a short column of phosphoric oxide.

The boat apparatus was provided with a manometer, registering up to 600 mm. pressure, which on account of its weight was attached at *c* by means of rubber tubing to the reaction bulb. The latter was moved up and down as before. The boat apparatus and as much as possible of the reservoir were put in a thermostat at 25°. The volumes of the reaction vessel and of the reservoir between *b* and *e* were known for all pressures.

In an experiment, the reservoir was charged with oxygen at a pressure about 300 mm. above the constant pressure required; 8 c.c. of a 97% solution of phosphoric acid and 0·5 g. of phosphorus trioxide were run into the reaction bulb and the apparatus was quickly evacuated between *a* and *d*. Tap *f* was closed and oxygen admitted to the evacuated bulb through tap *b* until the pressure was just below that required. The rate of inflow was controlled by means of the narrow capillary, *g*. When the apparatus had been 10 minutes in the thermostat, the pressure in the reaction vessel was carefully adjusted to the constant-pressure mark by admitting oxygen from the reservoir. Immediately after closing tap *b*, the time was noted and the pressure in the reservoir read off. Pressure in the reaction bulb was next allowed to fall not more than 5 mm. and then raised by admission of oxygen to about 5 mm. above the constant-pressure mark. The pressure fell again from this point, and the times of reaching the constant-pressure mark and the pressure of the reservoir were noted. Readings were made at intervals for 1½ hours or until the phosphorus trioxide was exhausted. From the change in PV, the product of the pressure and the volume of the reservoir, the amount of oxygen absorbed in a given time could be determined. For an experiment performed at 25° and at constant pressure (100 ± 4 mm.) the following results were obtained:

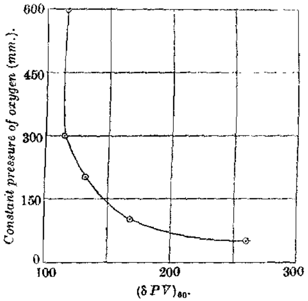
t (mins.).	P (cm.).	V (c.c.).	PV.	$(PV)_0 - (PV)_t = (\delta PV)_t$.
0	31·35	50·5	1583	0
7·5	31·0	50·5	1566	17
25	30·15	50·4	1520	63
29·5	29·9	50·4	1507	76
36	29·55	50·35	1487	96
42	29·2	50·3	1469	114
49	28·85	50·3	1451	132
57	28·35	50·25	1425	158
67	27·8	50·2	1395	188
75	27·4	50·15	1374	209
82·5	26·9	50·1	1348	235
90·5	26·4	50·1	1323	260

The change in PV in the time t, $(\delta PV)_t$, was equivalent to the volume of oxygen absorbed (in c.c. at 25° and 1 cm. pressure). Except for a slight initial retardation, the rate of absorption was

practically constant. Experiments performed with the pressure of oxygen constant at 600, 300, 200, and 50 mm. gave results of the same type, but showing different rates of absorption of oxygen. In order to compare the rates, the amount of oxygen absorbed in 60 minutes, $(\delta PV)_{60}$, was determined for each and the corresponding curve constructed (Fig. 3). It was unnecessary to correct for the change in volume of the reaction vessel with pressure, for the reaction only took place in the bulb part, which was the same for all.

An experiment at 25 mm. pressure was unsatisfactory, as the rate of oxidation on two occasions suddenly increased considerably. Fig. 3 indicates that the rate of oxygen absorption may become very great at pressures below 50 mm., an indication, probably, of ignition.

FIG. 3.



The results, which were all obtained with one specimen of phosphorus trioxide, showed that the rate of absorption of oxygen between 600 and 300 mm. pressure was practically constant but increased regularly as the pressure fell below 300 mm. This bore a resemblance to the rate of oxidation of phosphorus in moderately dried oxygen (see Russell, J., 1903, **83**, 1263).

In all experiments the position of the luminescence was striking. Bright flashing occurred principally below the boat, just above the acid surface, or at the end of the tube beyond the boat, *i.e.*, away from the source of phosphorus trioxide and near the water-vapour source. Attention has already been directed to the appearance of luminescence at sources of moisture at considerable distances from the oxide (Miller, *Proc. Roy. Soc. Edin.*, 1926, **46**, 239). Owing to the ease with which phosphorus trioxide took up water vapour in a

partially evacuated apparatus, it was difficult to imagine that in every instance phosphorus trioxide existed where luminescence appeared. Could the luminescence have been due to dissolved phosphorus? And if so, why did not luminescence appear at the surface of the liquid oxide as in the case of phosphorus dissolved in paraffin oil? The only explanation seemed to be that phosphorus trioxide prevented the luminescence of phosphorus. Phosphorus trioxide vapour containing phosphorus would therefore only luminesce if something were present to destroy the phosphorus trioxide. Water vapour, which is essential for the luminescence at the ordinary temperature, has this effect. One would then expect phosphorus trioxide to destroy the glow of slowly oxidising phosphorus. The following experiment was performed. Below the boat of the apparatus in Fig. 1, 5 c.c. of a solution of phosphorus in paraffin oil were introduced. Oxygen was present initially at 50 mm. pressure, and the solution glowed quite brightly at the surface. The pressure fell 29 mm. in 28 minutes. The experiment was started afresh, and after a minute 0·5 g. of phosphorus trioxide was run into the boat. The glow was immediately extinguished, and the pressure afterwards fell only 16 mm. in 170 minutes. This was not further studied, but the observation favoured the foregoing explanation that the glowing of phosphorus trioxide might be due to dissolved phosphorus.

Owing to its mode of preparation, the crude phosphorus trioxide contained phosphorus, which was no doubt partly removed by distillation. When the distillation proceeded too far, small globules of phosphorus accompanied the liquid phosphorus trioxide into the receiver and appeared not to dissolve to any extent. The phosphorus trioxide ordinarily used was therefore probably a saturated solution of phosphorus in phosphorus trioxide. Distillation over copper was not specially effective in removing phosphorus. Analysis, as previously mentioned, suggested the presence in the oxide of 1% of phosphorus. The well-known reddening of phosphorus trioxide in light has also been attributed to dissolved phosphorus. It is significant that the actual extent of decomposition is slight; for instance, Thorpe and Tutton (J., 1891, **59**, 1019) found only 1% of red phosphorus in a sample of oxide exposed for 7 months to light.

In order to determine the part, if any, played by phosphorus in the luminous oxidation of phosphorus trioxide, it was obvious that the preparation of a phosphorus-free oxide was desirable. An unsuccessful attempt was made to dehydrate pure phosphorous acid. In another attempt phosphorus trioxide was exposed to light in an evacuated bulb, and the oxide was volatilised from the red solid at 25° into a second bulb where it was again exposed. Reddening occurred as before and the process was once more repeated. The

reddening effect was purely a superficial one. The light seemed to affect the white, opaque phosphorus trioxide, not the transparent crystals which sometimes formed. If the latter were melted and resolidified, they gave a white opaque solid which was affected by light. As there was apparently no diminution in the amount of reddening in the third bulb, this attempt to separate phosphorus was abandoned.

The next method adopted was the recrystallisation of freshly distilled phosphorus trioxide from a suitable solvent. Carbon disulphide is by far the best solvent for phosphorus but phosphorus trioxide also dissolves readily. A preliminary trial showed, however, that it could be employed if the temperature of recrystallisation was about $-18°$ and the amount used was small. The solvent was dried and distilled over mercury before use. Carbon disulphide is known to be a strong inhibitor of the glow of phosphorus, but it was found that there was no diminution of the glowing of a specimen of phosphorus trioxide after it had been dissolved in carbon disulphide and the solvent removed by evaporation, finally with the aid of a pump.

The Recrystallisation of Phosphorus Trioxide.—As a trial a small quantity of freshly distilled phosphorus trioxide was recrystallised four times from carbon disulphide in an atmosphere of carbon dioxide. The solvent was then expelled by a fairly rapid stream of carbon dioxide, and the purified oxide, about 25% of the original bulk, transferred to a boat apparatus (Fig. 1) and oxidised at 25° in presence of a 97% solution of phosphoric acid and oxygen at a constant pressure of 100 mm. (compare p. 1851). At first no glowing was seen, but after a time there were occasional bright flashes without pressure change in 50 minutes. It was suspected that a trace of carbon disulphide was responsible for the lack of oxidation. The apparatus was therefore re-evacuated and fresh oxygen passed in. Slight glowing occurred and the pressure fall corresponded to $(\delta PV)_{40} = 5{\cdot}2$. After a further evacuation and addition of oxygen the pressure fall was practically the same. The rate of oxidation of ordinary distilled phosphorus trioxide was previously found to be represented by $(\delta PV)_{40} = 108$ (see table, p. 1852), therefore the rate of oxidation of the purified oxide was reduced to one-twentieth of the original, probably corresponding to a similar reduction in the amount of dissolved phosphorus. The phosphorus trioxide obtained from the mother-liquor was found to oxidise at the normal rate.

These results showed that greater care had to be taken in eliminating solvent from the purified oxide. The apparatus shown in Fig. 4 was designed for recrystallisation experiments. It consisted

of a flat-bottomed tube provided with a side tube through which the mother-liquor from the crystals could be poured. It was further provided with a rubber stopper holding a small tap-funnel, and with a glass rod to which was attached by platinum at the lower end a perforated porcelain disc of nearly the same diameter as the tube. The disc could be moved up and down the tube like a piston. Dry carbon dioxide was passed into the apparatus as shown. Freshly distilled phosphorus trioxide and carbon disulphide were mixed by stirring in the tube and cooled to $-18°$, the perforated disc being moved up and down to prevent formation of crystals

FIG. 4.

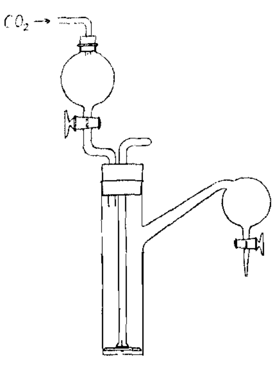
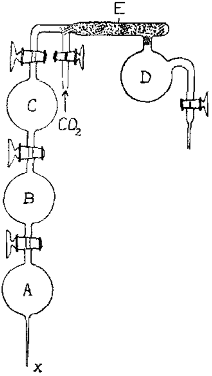


FIG. 5.



on the walls. The crystals were then allowed to settle and the disc was pressed down to force out the liquor. The latter was quickly poured off into the side bulb and thence removed. The recrystallisation was repeated and the crystals were finally washed with cooled carbon disulphide. The purified oxide was melted, transferred to a small tube, and solvent removed by evacuation with an oil pump, the oxide meanwhile being many times melted and resolidified. The yield of oxide was slightly higher than before. The specimen glowed when rubbed on the fingers, and in ozonised oxygen, but did not ignite on cotton wool. When oxidised according to the usual method the amount of oxygen absorbed was $(\delta PV)_{40} = 9$, slightly more than before, and there was quite bright flashing at intervals.

The maximum amount of oxygen absorbed by this oxide corresponded to little more than 0·1% of dissolved phosphorus.

Light petroleum (b. p. 40—60°) was tried in case the preceding results were due to carbon disulphide. Recrystallisation was effected five times and the solvent removed as before. The amount of oxygen absorbed by a portion of the oxide was equivalent to $(\delta PV)_{40} = 27$, three times the value found above. If the oxidation was due to phosphorus alone, this result indicated that there was three times as much phosphorus left in the oxide as in the preceding experiment and one-quarter of the amount present in the ordinary distilled oxide for which $(\delta PV)_{40}$ was 108. One might expect to obtain identical results for the rate of absorption of oxygen by the three specimens of phosphorus trioxide obtained by saturating the two purified oxides and the unpurified oxide (if not already saturated) with phosphorus at 25°. For the first two the values of $(\delta PV)_{40}$ were found to be 92 and 90, and for the last, 100. The two lower values were attributed to the fact that only minimum quantities of the solutions were prepared and phosphorus separated slightly while the oxides were being measured out. This did not happen with the third specimen. The value 100 was lower than that previously obtained for phosphorus trioxide, *viz.*, 108. The latter value was due to the use of oxide melted at 30—40°, which contained sufficient phosphorus to saturate it at a temperature above 25° and more than enough to saturate it at 25°.

The recrystallisation of a much larger quantity of phosphorus trioxide was attempted. Light petroleum was apparently not so effective as carbon disulphide in removing phosphorus, but it had the advantage that larger quantities could be used. A combination of methods was therefore adopted, the recrystallisation being effected with carbon disulphide and the crystals washed with light petroleum. 40 C.c. of freshly distilled phosphorus trioxide were mixed with one-third of the volume of pure carbon disulphide and recrystallised at −18°. The crystals were pressed as free as possible of liquor and washed with 15 c.c. of cooled light petroleum. The process was twice repeated with diminishing quantities of the solvents, and followed by two final washings with light petroleum (5 c.c. and 10 c.c.). The crystals were melted and filtered through glass-wool into a bottle from which air was displaced by dry carbon dioxide. The yield was about one-third of the original bulk.

The oxide in the mother-liquors was recovered, excess of phosphorus removed, and the oxide distilled and recrystallised as before. In all, three products were obtained and put in one bottle from which the remaining solvent was carefully removed as before. The phosphorus trioxide in the last mother-liquor was recovered from

solution in the usual manner and distilled in a vacuum to give a clear phosphorus-saturated solution of phosphorus trioxide.

A little of the purified oxide was oxidised in presence of 4 mm. of water vapour. The total amount of oxygen absorbed corresponded to about 0·02% of dissolved phosphorus. Bright flashing occurred under the boat during the first ½ hour; after 3 hours no glowing was seen and the pressure remained steady. This experiment indicated further removal of phosphorus from the oxide. A drop of this purified material when rubbed on the fingers gave a bright but momentary glow, whereas a drop of the ordinary oxide gave a glow sufficiently bright and lasting to illuminate the whole hand. It was supposed that the purified oxide glowed and absorbed a minute quantity of oxygen because of the retention of a trace of phosphorus. Elimination of this trace by further recrystallisation was impracticable, but it was thought that it might be eradicated by exposure of the oxide to sunlight, a process in which there was no further introduction of substances with an inhibitory effect on the glow. According to expectations the oxide reddened in sunlight, but not to the extent shown by the unpurified oxide. The apparatus shown in Fig. 5 was designed. Initially only that part was used which consisted of the three glass bulbs joined together as indicated. Phosphorus trioxide was drawn into bulb *A* and *x* was sealed off. The three bulbs were then thoroughly evacuated and the taps closed. As large a surface as possible of the phosphorus trioxide was exposed to light for a few hours and considerable reddening took place. The apparatus was re-evacuated and the phosphorus trioxide in bulb *A* volatilised into bulb *B* by heating *A* to 40° and cooling *B*. The oxide was again exposed to light, whereupon further reddening occurred, and then transferred to bulb *C* for a third exposure. In bulbs *B* and *C* the reddening was not so extensive as in bulb *A*. The second part of the apparatus, which had not been contaminated with phosphorus trioxide vapour containing phosphorus, was now sealed on to the three bulbs, and the tube *E* charged with phosphoric oxide. The whole apparatus was evacuated and the phosphorus trioxide in bulb *C* volatilised through the phosphoric oxide into the receiving bulb *D*. The drying tube and the bulb *D* were then filled with pure, dry carbon dioxide to atmospheric pressure, and portions of the oxide removed as required.

The Properties of Purified Phosphorus Trioxide.—1. At the ordinary temperature the oxide was a transparent, crystalline solid, lacking the opaque, waxy appearance of the unpurified product, caused probably by the separation of phosphorus from solution, on solidification.

2. A clear, colourless sample of purified phosphorus trioxide

contained in an evacuated bulb was exposed to light for 10 weeks in a well-lit laboratory, but, although it was several times melted and resolidified, it remained colourless and transparent. Crude phosphorus trioxide similarly treated was readily affected by light (see p. 1854). A second sample of purified oxide, which was kept in an atmosphere of carbon dioxide and used for the following experiments, was also exposed to light. The colourless crystalline mass assumed, during the first few hours' exposure, a faint pink tinge which did not deepen on further exposure for 6 weeks. The colour was due to the separation of a very small quantity of red substance.

3. When rubbed on the fingers the purified oxide gave no glow, and for a short time there was a pungent acid smell resembling that of hydrochloric acid. The phosphorus smell so readily detected with ordinary phosphorus trioxide was entirely absent. The pure oxide when spread on cloth did not ignite as does the ordinary product, but when mixed with a small proportion of the crude oxide, or with phosphorus, glowing and ignition were restored.

4. The m. p.'s of the purified and unpurified oxides were determined in a vacuum in small melting-point tubes, the oxide in each case having been initially volatilised through phosphoric oxide. The values found were: Purified oxide, 23·8°; unpurified oxide, 22·4°.

5. In order to obtain an indication of the amount of phosphorus dissolved in the unpurified oxide, the depression constant of the pure oxide was found by determining by Rast's method (*Ber.*, 1922, **55**, 1051) the lowering of freezing point produced by naphthalene as solute. With solutions containing 1·98 and 2·67% of naphthalene the lowerings were 1·85° and 2·4° respectively, giving for the depression constant the values 11,700 and 11,200. For the lowering of freezing point produced by phosphorus, *viz.*, 1·4°, a depression constant of 11,000 gives 1·6 g. as the amount of phosphorus (as P_4) dissolved in 100 g. of trioxide.

6. The pure oxide and the oxide saturated with phosphorus at 25° were analysed quantitatively: 0·15—0·25 g. was melted under water in a small flask and heated at 40—50° till converted into phosphorous acid. The pure oxide left no residue, whereas the unpurified oxide left a residue of phosphorus. An excess of liquid bromine was added and then 3—4 c.c. of 4*N*-sodium hydroxide, since hypobromite is known to oxidise phosphorous acid. Phosphorus was also completely oxidised. After a short time 5 c.c. of concentrated nitric acid were added and the solution was boiled to free it from bromine. The phosphoric acid was precipitated twice as magnesium ammonium phosphate, which was converted into pyrophosphate

(Found, for purified oxide: 100·04, 100·05; for unpurified oxide: 101·37, 101·47%). On the assumption that the purified oxide was entirely free from phosphorus, the last two results correspond respectively to 1·74 g. and 1·87 g. of free phosphorus in 100 g. of trioxide.

7. The solubility of phosphorus in the purified oxide at 25° was determined by shaking a weighed excess of purified phosphorus with about 1 g. of phosphorus trioxide in a small stoppered tube, in an atmosphere of carbon dioxide. The tube was first heated sufficiently to melt the phosphorus and then allowed to stand at 25°. The excess of phosphorus collected into a globule which was easily removed, washed, and weighed. The weight of phosphorus dissolved corresponded to 1·71 g. per 100 g. of trioxide. Experiments 5, 6, and 7 therefore showed satisfactory agreement.

8. The behaviour of the purified oxide in oxygen was studied. At 25° and in presence of 4 mm. of water vapour, the oxide neither glowed nor absorbed oxygen at 100 mm. or 18 mm. pressure, in contradistinction to the absorption of oxygen, accompanied by luminescence, exhibited by impure phosphorus trioxide (see Expt. 3, p. 1859). In presence of concentrated sulphuric acid it gave no deposition of oxides at 25° in oxygen at 600 mm. pressure, whereas unpurified phosphorus trioxide, under similar conditions, deposited phosphorus tetroxide (see Miller, *Proc. Roy. Soc. Edin.*, 1926, **46** 239). At higher temperatures, the following phenomena were noticed. 0·2—0·3 G. of oxide was mixed with phosphoric oxide and volatilised into a 6 c.c. bulb into which pure dry oxygen was passed to a pressure of 300 mm. The bulb was sealed and heated gradually, but no glowing or fuming was seen below 200°. At about 220°, fuming was observed, accompanied by a very faint glow. The action was not brisk, for after ½ hour's heating at this temperature oxygen was still present. With undried phosphorus trioxide and moist oxygen the result was much the same, but in a second similar experiment oxidation appeared at 130°. Unpurified phosphorus trioxide gave an entirely different result, igniting at 40° in dry oxygen at 300 mm. pressure and using up all the oxygen. When ozonised oxygen containing 1% of ozone was passed at a slow rate over the pure phosphorus trioxide at 25°, oxidation occurred without luminescence. Under similar conditions, ordinary phosphorus trioxide glowed brightly and difficulty was experienced in preventing ignition.

9. When the purified oxide was melted under excess of water and heated gradually, it was simply converted into phosphorous acid, until a temperature of 75—80° was reached. At this point decomposition set in, bubbles of gas passed up through the water

from the oxide, and yellow and red solid products were formed. The gas fumed at the surface of the water and gave bright flashes. Unpurified phosphorus trioxide exhibited the same phenomena at a somewhat lower temperature.

When purified phosphorus trioxide in excess was sealed in an evacuated bulb with a small quantity of water, a clear yellow syrup formed, which after several days became opaque. The bulb was opened under water, but no gas was present. The amount of yellow solid was so small that accurate analysis was impossible—it is possibly a suboxide.

10. When the purified oxide was heated in a vacuum at 300°, red, yellow, and white decomposition products were formed, phosphorus tetroxide being amongst them. The thermal decomposition of ordinary phosphorus trioxide gives a similar result.

11. A portion of the pure trioxide was saturated with purified phosphorus at 25°. The oxide so obtained assumed on solidification the white, opaque appearance of unpurified phosphorus trioxide, glowed in air, ignited on cloth, and reddened in light.

Summary.

A study of the rate of absorption of oxygen by phosphorus trioxide in presence of water vapour at various pressures led to the conclusion that the luminescence of the oxide was essentially connected with the presence of dissolved phosphorus.

Phosphorus trioxide, as prepared by Thorpe and Tutton's method, invariably contained phosphorus, the bulk of which could be removed by several low-temperature recrystallisations from carbon disulphide. The remainder was removable by exposure of the oxide to light and subsequent volatilisation from the red product.

The pure oxide so obtained melted at 23·8°, *i.e.*, 1·4° higher than the unpurified product, and lacked many of the properties formerly attributed to phosphorus trioxide. For instance, it neither glowed nor oxidised in moist or dry oxygen at the ordinary temperature and was unaffected by sunlight. When it was heated in a sealed bulb with dry oxygen at 300 mm. pressure, fuming and very faint glowing were observed at about 200°. By addition of pure phosphorus to the pure oxide the properties previously regarded as characteristic of phosphorus trioxide were restored.

The trioxide was found to dissolve 1·7 g. of phosphorus per 100 g. when saturated at 25°.

It is not yet known if the absorption of oxygen by the impure oxide is due to phosphorus alone or to phosphorus and phosphorus trioxide together, but this point is being investigated.

A study of the oxidation products of phosphorus in oxygen and

of phosphorus trioxide in oxygen and ozonised oxygen is being continued.

The author wishes to thank Professor Sir James Walker, F.R.S., for the interest he has taken and the encouragement he has given her in the prosecution of this investigation.

UNIVERSITY OF EDINBURGH. [*Received, May 19th*, 1928.]

CCXLI.—*The Action of Fluorine upon Aqueous Solutions of Chromium and Manganese Salts.*

By FRIEDRICH FICHTER and ERNST BRUNNER.

OUR researches on electrochemical oxidation of organic compounds have fully demonstrated the efficiency of a platinum anode as a powerful oxidising agent, and we noted especially the formation of organic peroxides and peracids, which are the intermediate products in the different forms of the Kolbe reaction. Since this effect is to be attributed to oxygen formed under a very high potential, and since there is no fundamental difference between electrochemical oxidation and ordinary chemical oxidation, we anticipated that similar results could be achieved by purely chemical means if the reagents furnished oxygen of the same high potential.

The positive end of the table of electrochemical potentials (first supplement, Deutsche Bunsen-Gesellschaft, 1915), measured in *N*-solutions of the respective salts, represents a number of such oxidising agents, several of which (*e.g.*, hydrogen peroxide, quadrivalent lead, and ozone) are frequently employed :

Lower stage of oxidation.		Higher stage of oxidation.	Potential.
$2H_2O$	$\longrightarrow$	$H_2O_2 + 2H^{\cdot}$	+ 1·8 volts
$Co^{\cdot\cdot}$	$\longrightarrow$	$Co^{\cdot\cdot\cdot}$	+ 1·8 ,,
$Pb^{\cdot\cdot}$	$\longrightarrow$	$Pb^{\cdot\cdot\cdot\cdot}$	+ 1·8 ,,
$O_2 + H_2O$	$\longrightarrow$	$O_3 + 2H^{\cdot}$	+ 1·9 ,,
$2F'$	$\longrightarrow$	F_2	+ 1·9 ,,

The figures in the table are somewhat uncertain, and the value for fluorine is probably too low. Von Wartenberg (*Z. anorg. Chem.*, 1926, **151**, 313) has recently found that the heat of formation of 1 g.-mol. of hydrogen fluoride in aqueous solution is equal to 74·6 Cal., instead of 50·3 Cal., the generally adopted value of Berthelot and Moissan. Latimer (*J. Amer. Chem. Soc.*, 1926, **48**, 2868) estimates the potential of gaseous fluorine to be as high as + 2·85 volts, direct measurements being impossible, since fluorine reacts instantaneously with water.

In spite of the well-known and powerful chemical affinity of

fluorine, its effect upon aqueous solutions of mineral salts does not appear to have been examined by Moissan, and even Ruff, who used gaseous fluorine in the preparation of the highest fluorides of the platinum metals, does not mention its use in this way.

Our assumption that fluorine, owing to its position in the potential table, would act as the most powerful oxidising agent proved to be correct, for we have prepared crystalline potassium and ammonium persulphates by its action upon the corresponding bisulphates, and perphosphates, percarbonates, and perborates in a similar way (*Helv. Chim. Acta*, 1923, **6**, 640; 1926, **9**, 467; 1927, **10**, 549). The oxidising power of fluorine is, therefore, at least equal to that of a platinum anode. The formation of persulphates from bisulphates might be written as $2KHSO_4 + F_2 = K_2S_2O_8 + 2HF + 42{\cdot}6$ Cal., or as $2SO_4'' + F_2 = S_2O_8'' + 2F'$. If we adopt the first equation, we should write the electrochemical formation of persulphates in a similar way: $2KHSO_4 + O = K_2S_2O_8 + H_2O$, whereas the usual explanation emphasises the ionic reaction $2SO_4'' = S_2O_8'' + 2\ominus$. The difference between the two conceptions is purely formal.

The oxidising power of fluorine, however, surpasses that of a platinum anode, for by introducing it into sulphuric acid of medium concentration we obtain sulphur tetroxide ($H_2SO_4 + F_2 = SO_4 + 2HF$), a very labile compound which exists only a few hours and decomposes with evolution of ozone. Berthelot had previously obtained this tetroxide by treating a mixture of sulphur dioxide with excess of oxygen in an ozoniser. Our method gives better yields, but the tetroxide cannot be isolated from its solution. The production of ozone in the electrolysis of concentrated sulphuric acid with platinum anodes must, apparently, be explained by the intermediate formation of the same labile sulphur tetroxide.

These reactions of fluorine upon acids or anions are capable of wide extension, for we have recently found that nitric and perchloric acids furnish extremely labile peroxides or peracids. We now describe the action of fluorine upon kations of a lower valency.

Marshall discovered that a well-cooled solution of cobaltous sulphate in sulphuric acid gives, by electrolysis, the sulphate of tervalent cobalt (J., 1891, **59**, 760), and Fichter and Wolfmann (*Helv. Chim. Acta*, 1926, **9**, 1093) prepared the same salt by passing fluorine into a solution of cobaltous sulphate in sulphuric acid. The latter noted that in such cases the anion of the salt is of importance, for only the sulphate can be thus oxidised and the concentration of free sulphuric acid has to be kept between certain limits. Although this preparation of cobaltic sulphate requires a relatively high concentration of sulphuric acid, no mechanism other than the

orthodox ionic explanation ($2Co^{\cdot\cdot} + F_2 = 2Co^{\cdot\cdot\cdot} + 2F'$) has hitherto been suggested, but we prefer the hypothesis that the labile sulphur tetroxide, formed by interaction of fluorine and sulphuric acid, is the true oxidising agent: $2CoSO_4 + SO_4 = Co_2(SO_4)_3$.

Our experiments with chromium salts corroborate this conception. A solution of chromium alum, acidified with very dilute sulphuric acid, is not altered by the passage of fluorine for several hours, but if the concentration of free acid is as high as $1{\cdot}5N$, a regular oxidation to chromic acid sets in, and is easily recognised by the change of colour from violet to orange-yellow. Higher concentrations of sulphuric acid up to $7{\cdot}5N$ have the same effect. The oxidation is certainly indirect, for if the amount of chromic acid is determined by titration, the fresh solution, which evolves ozone, has about 1·5 times the possible oxidising power. After standing over-night or heating on a water-bath, the excess of oxidising substances is destroyed, and the solution has an oxidising value corresponding exactly to the theoretical amount of chromic acid. The oxidising substance must be sulphur tetroxide, for it is effective at 0°, whereas persulphate oxidises chromic salts only at higher temperatures.

We may conclude from these experiments that the electrochemical oxidation of chromium alum to chromic acid is also an indirect one. Since it is essential that the sulphuric acid be concentrated (Höchster Farbwerke, D.R.-P. 103,860, 1898), we suggest that this is because the acid must be strong enough to furnish sulphur tetroxide.

If a dilute solution of potassium dichromate is treated with fluorine, it becomes green and is reduced to a chromic salt, most probably the fluoride. Our crude fluorine always contains free hydrogen fluoride; the action of fluorine upon an aqueous solution furnishes hydrofluoric acid, and its concentration would be sufficient for the formation of chromic fluoride. In this case, fluorine acts as a reducing agent. This contradictory behaviour must be explained by the intermediate formation of hydrogen peroxide, thus: $2H_2O + F_2 = H_2O_2 + 2HF$. The formation of hydrogen peroxide can be detected by working with a small quantity of chromic acid and in the presence of dilute sulphuric acid; under these conditions and by proper cooling we obtain the blue perchromic acid, soluble in ether. Perchromic acid is very unstable, losing oxygen and yielding chromic salts; in this manner the reduction of dichromate can be carried out quantitatively by prolonged treatment with fluorine.

The concentrated sulphuric acid used in the oxidation of chromium alum to chromic acid fulfils two functions: first, it furnishes the sulphur tetroxide, the true oxidising agent, and, secondly, it prevents

the formation of hydrogen peroxide, and hence of perchromic acid which would lead to reduction.

Both reactions which chromium compounds undergo under the influence of gaseous fluorine must be explained by intermediate products formed by the action upon water or sulphuric acid. Consequently, in oxidations with fluorine, an excess of this gas is often detrimental, for it destroys, by secondary reactions, the substances which it formed first.

The electrochemical oxidation of manganese salts has been investigated by several authors (see a review by Sem, *Z. Elektrochem.*, 1915, **21**, 425). As the action of fluorine is in most cases a true counterpart of electrochemical oxidation, we directed our attention to the similarity as well as to the difference of the two methods.

When a suspension of manganous fluoride in water is treated with a stream of fluorine, it dissolves slowly, furnishing a red liquid, from which a saturated solution of potassium fluoride precipitates the complex potassium manganifluoride, K_2MnF_5,H_2O (discovered by Christensen, *J. pr. Chem.*, 1887, **35**, 57), a pink crystalline powder. In this case, we admit the possibility of a direct oxidation without formation of an intermediate product; but the reaction is far from being complete: the formation of hydrogen peroxide can be detected from the beginning, and, moreover, we have a complicated equilibrium between manganous and manganic fluorides, hydrofluoric acid, and hydrogen peroxide, where the temperature, concentration, and duration of the treatment with fluorine are of influence. Sometimes the pink colour diminishes even during the experiment.

The formation of manganese tetrafluoride proved to be impossible by this method.

In most cases we used platinum vessels for our experiments, but the metal appeared to have a catalytic effect in decomposing salts of high valency (compare hydrogen peroxide), especially when it had lost its smoothness. To avoid this danger, we employed graphite beakers, but even with this precaution it was impossible to obtain manganese tetrafluoride. Further, a solution of the yellow complex salt, K_2MnF_6 (Weinland and Lauenstein, *Z. anorg. Chem.*, 1899, **20**, 40), was immediately reduced to the red salt by fluorine. This inability of fluorine to oxidise manganous fluoride to manganese tetrafluoride is completely parallel to the failure to effect this reaction by anodic oxidation (Mueller and Koppe, *ibid.*, 1910, **68**, 160).

Manganous sulphate, in the presence of sulphuric acid, was more readily oxidised, undoubtedly owing to the intervention of sulphur tetroxide. The formation of manganic sulphate, the first step, is

easy to recognise, by the red colour. On continued passage of fluorine, this colour changes to a brownish-red and finally to a dark brown, and the oxidising power corresponds to a nearly complete transformation into the labile sulphate of quadrivalent manganese, $Mn(SO_4)_2$. If the concentration of the sulphuric acid is not high, hydrolysis sets in, and manganese dioxide is formed; but, although it is easy to obtain a yield exceeding 90%, the formation of manganese dioxide is not a certain proof of the primary formation of a salt of quadrivalent manganese, for it may be formed by hydrolysis of manganic sulphate, one-half of which is reduced to manganous sulphate and subsequently re-oxidised.

In order to bring the oxidation to the highest stage, permanganic acid, it is useful to have a low concentration of manganous ions and a high concentration of sulphuric acid, the latter being necessary to avoid the formation of hydrogen peroxide. In these circumstances, the characteristic colour of permanganate ions becomes visible the more quickly the smaller the concentration of manganous sulphate.

Manganic phosphate is very stable; a strong solution of manganous carbonate in an excess of phosphoric acid turns a deep amethyst-red on treatment with fluorine, but the oxidation is not complete. This is easy to understand, for the solution contains traces of hydrogen peroxide. We assume that fluorine acts first upon the phosphoric acid, forming monoperphosphoric acid, which readily oxidises manganous sulphate in acid solution to manganic phosphate. Schmidlin and Massini, who first prepared monoperphosphoric acid, considered the amethyst colour to be due to permanganic acid (*Ber.*, 1910, **43**, 1166), but spectrographic examination shows at once that the dark lines are lacking.

All the experiments with manganese salts and fluorine correspond exactly with the results of electrochemical oxidations. In all cases fluorine has proved to be at least as powerful an oxidising agent as a platinum anode, and our observations throw a new light on the mechanism of such oxidations, which are by no means simple. They depend largely on the anions, and also on intermediate products formed by primary oxidation of the acids, which are ignored in the theory of augmentation of positive charges (see p. 1864).

EXPERIMENTAL.

For the sake of brevity, we give for each reaction only one out of the great number of experiments carried out. (Fuller details will be published in E. Brunner's thesis.)

A. *Chrome Alum and Fluorine.*—(1) 0·9734 G. of chrome alum, 50 c.c. of water, and 2 c.c. of concentrated sulphuric acid were placed in a platinum crucible, cooled with ice, and treated with a current

of fluorine during 75 minutes. The solution became orange and evolved ozone. After addition of potassium iodide and starch solution, 84·17 c.c. of 0·1*N*-thiosulphate solution were needed; this corresponds to 0·2808 g. of CrO_3, whereas the possible maximum is only 0·1949 g.

(2) 1·1365 G. of the alum and the above amounts of water and acid were treated as before. After standing over-night and being heated on the water-bath, the solution was mixed with potassium iodide and titrated with 0·1*N*-thiosulphate solution (Found: 0·2281 g. CrO_3. Calc.: 0·2276 g.).

B. *Potassium Dichromate and Fluorine.*—(1) *Formation of perchromic acid.* One drop of 0·5*N*-potassium dichromate, 40 c.c. of water, and 5 c.c. of 2*N*-sulphuric acid were placed in a platinum crucible, carefully cooled with ice and salt, and a few bubbles of fluorine introduced. By shaking with ether, previously freed from organic peroxides, the dark blue colour of perchromic acid was extracted.

(2) *Reduction to chromic fluoride.* 0·5216 G. of dichromate was dissolved in 50 c.c. of water, and, after cooling in ice, treated during 3 hours with fluorine. The green solution was partly evaporated in a platinum dish on the water-bath and then precipitated by ammonia; it furnished 0·2664 g. of chromium oxide (Calc.: 0·2695 g. Yield 98·9%).

C. *Manganous Fluoride and Fluorine.*—(1) Manganese fluoride was suspended in water, by a stirrer, in a platinum crucible, and treated with fluorine until nearly all was dissolved; the unattacked fluoride was removed by filtration through a hardened filter in a paraffined funnel, and the clear solution mixed with a saturated solution of potassium fluoride, whereupon a pale red crystalline powder separated, which was washed with very dilute hydrofluoric acid and dried at room temperature (Found: Mn, by conversion into Mn_3O_4, 22·37; active F, 7·67. Calc. for K_2MnF_5,H_2O: Mn, 22·32; active F, 7·72%).

(2) 0·6384 G. of manganous fluoride, suspended in water, cooled in ice, and treated during 1½ hours with fluorine, dissolved and became red. After addition of potassium iodide and hydrochloric acid, it required 48·02 c.c. of 0·1*N*-thiosulphate solution, *i.e.*, yield = 69·9%.

D. *Manganous Sulphate and Fluorine.*—(1) *Formation of manganese dioxide.* 10 C.c. of a 1·11*N*-solution of manganous sulphate, with 0·3039 g. of $Mn^{\cdot\cdot}$, were treated exactly as in C(2); the solution remained colourless, but manganese dioxide was precipitated. Both the solution and the precipitate were distilled with hydrochloric acid, and the evolved chlorine was passed into a

solution of potassium iodide. The liberated iodine consumed 101·2 c.c. of 0·1*N*-thiosulphate solution. If the manganous salt had been transformed completely into dioxide, 110·6 c.c. would have been needed; the yield was therefore 91·5%.

(2) *Formation of the sulphate of quadrivalent manganese.* A mixture of 2 c.c. of a 1·11*N*-solution of manganous sulphate, with 0·0608 g. of $Mn^{\cdot\cdot}$, and 4·0820 g. of concentrated sulphuric acid (95·64%) was cooled in ice and treated with fluorine during 5 hours; it became red, then browner, and finally dark brown. Concentrated hydrochloric acid and potassium iodide were added and the iodine was titrated [Found: 19·2 c.c. Calc.: 22·1 c.c. Hence yield of $Mn(SO_4)_2$ = 86·9%]. This result is probably too high, for the solution may have contained sulphur tetroxide in addition to quadrivalent manganese.

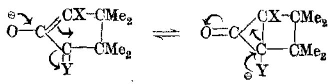
(3) *Formation of permanganic acid.* Three drops of a 1·11*N*-solution of manganous sulphate, 10 c.c. of water, and 3·3902 g. of concentrated sulphuric acid (95·64%) were treated with fluorine. After 15 minutes, the violet colour of permanganic acid appeared and became more and more distinct; the spectroscope revealed clearly the five absorption bands. With two drops of the manganous sulphate solution the violet colour appears after a few minutes; with four drops a treatment of one hour is needed, but the colour becomes very rich.

THE UNIVERSITY, BASLE. [*Received, May 31st, 1928.*]

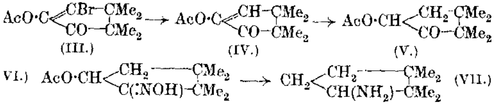
CCXLII.—*On the Possibility of Ring-chain Valency Tautomerism, and of a Type of Mobile-hydrogen Tautomerism analogous to the Wagner–Meerwein Re-arrangement. Part III. Orientation of some Cyclic Derivatives of Phorone.*

By CHRISTOPHER KELK INGOLD and CHARLES WILLIAM SHOPPEE.

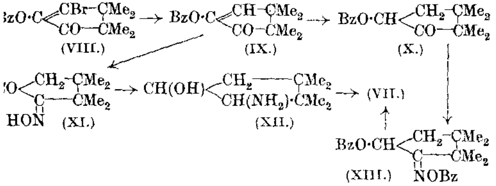
FRANCIS and WILLSON (J., 1913, **103**, 2238), who first examined the cyclic derivatives of phorone, ascribed formulæ of type II, but in Part I (this vol., p. 365) it was shown that formulæ of type I are also necessary in order fully to account for the reactions of the substances.

(I.)  (II.)

Amongst the derivatives studied in Part I was a series of acyl ınd alkyl derivatives of "bromohydroxyphorone" and hydroxy-)horone (X = H, Br; Y = O). The acetoxy- and methoxy- 'ompounds were definitely shown to have structure I, and this has ıow been confirmed as regards the acetoxy-derivatives (III) and IV) by the preparation of the crystalline *oxime* (VI) of the dihydro- ompound (V): the oxime, on complete reduction, yields 2 : 2 : 3 : 3- etramethyl*cyclo*pentylamine (VII).



The benzoyloxy-derivatives (VIII) and (IX) were not definitely riented in the previous communication, but a number of reactions 'ere studied, and of these the most significant is the formation of n oxime, to which formula (XI) was assigned, from the benzoyloxy- ompound (IX) with extrusion of the benzoyl group.

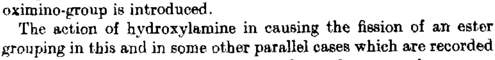


The reaction was illustrated by means of Francis and Willson's ›rmula, but it was pointed out that definite structural conclusions ɔuld not be reached without knowledge as to whether the oximino- roup enters the same position as, or another position than, that from 'hich the extruded benzoyl group had been removed. This point as now been elucidated. In the first place, the constitution ssigned to the oxime has been confirmed by reduction *via* the ydroxy-amine (XII) to 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine ⁄II). Secondly, the benzoyloxy-compound, although unaffected ɔth by zinc and by sodium amalgam in acetic acid, was successfully ıduced to a dihydro-derivative (X) by means of hydrogen in the :esence of palladised barium sulphate. This compound is identical ith the more fusible benzoyl derivative of tetramethyl*cyclo*- ɜntanolone, described in Part II (this vol., p. 1662), in which the ›nstitution of the derivative was definitely established by the

conversion of its benzoyloxime (XIII) into 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine. These reactions show that the benzoyloxy-bromo- and benzoyloxy-compounds possess the structures (VIII) and (IX) and that in the oximination of the latter the benzoyl group is extruded from another position than that into which the oximino-group is introduced.

The action of hydroxylamine in causing the fission of an ester grouping in this and in some other parallel cases which are recorded in the experimental portion appears to be analogous to the process of hydrolysis, and we have confirmed the fact that hydroxylamine may exhibit this action on simple substances by showing that phenyl benzoate is broken down into phenol and benzoic acid by boiling with hydroxylamine in alcohol.

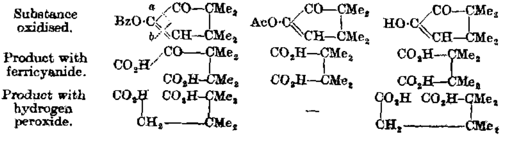
Investigation of the *p*-bromobenzyloxybromo- and *p*-bromobenzyloxy-compounds (XIV) and (XV) has shown that these possess structures similar to those of the benzoyl derivatives. The *p*-bromobenzyloxy-compound (XV) is extremely resistant to reduction and it had been found (this vol., p. 376) to yield an oxime (XVI) which, when reduced, gave a hydroxy-amine isomeric with that obtained by reduction of the oxime (XI). The former hydroxy-amine has now been reduced to 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine and must therefore be a geometrical and not a position isomeride.



(XIV.) (XV.) (XVI.)

($R = C_7H_6Br$.)

Part I recorded a study of the oxidation of hydroxybromo- and hydroxy-phorone and certain derivatives, and it was suggested that the observations could best be interpreted on the assumption that the monocyclic unsaturated forms of these substances could undergo oxidative fission in two directions (*a*) and (*b*) (formulæ below). These studies have now been extended with results which are shown in the table below and appear to suggest that the normal mode of fission produced by oxidation with potassium ferricyanide is at (*b*) whilst fission with hydrogen peroxide occurs preferentially at (*a*).



Experimental.

*5-Acetoxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanoneoxime* (VI).—The pure dihydroacetoxy-derivative, b. p. 120—121°/10 mm. (3·0 g.), hydroxylamine hydrochloride (1·2 g.), and anhydrous sodium acetate (1·4 g.) were heated together in absolute alcoholic solution on the steam-bath for 3 hours. On pouring the product into water, an oil was precipitated, the ethereal extract of which was washed with sodium hydrogen carbonate solution, dried, and evaporated. The pale yellow oil obtained did not crystallise after being kept for 2 months; the ethereal solution was therefore treated with dry hydrogen chloride at 0°, and the *oxime hydrochloride* was obtained as a colourless crystalline solid, m. p. 136—137° (with evolution of hydrogen chloride).

Solution in 2*N*-sodium carbonate and extraction with ether yielded the *oxime* as a rapidly solidifying oil. It separated from ligroin (b. p. 40—60°) in well-formed prisms, m. p. 93° (Found: C, 61·9; H, 9·2. $C_{11}H_{19}O_3N$ requires C, 62·0; H, 9·0%).

Reduction of the oxime (VI). The oxime (1·0 g.) was reduced with 2½% sodium amalgam (50 g.) by the method given in Part I (this vol., p. 393), and the product identified as 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine.

Reduction of the oxime (XI). The oxime was first reduced in the usual manner with sodium amalgam and glacial acetic acid; the basic portion of the product was then boiled with hydriodic acid (*d* 1·7) and red phosphorus under reflux for 2 hours. The product was distilled in steam, the distillate being disregarded; the contents of the flask were then made strongly alkaline and again steam-distilled. The ethereal extract of the distillate, dried with anhydrous potassium carbonate, was evaporated to small bulk under a column, and treated with ethereal picric acid. The resulting picrate was identified as that of 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine.

*Reduction of 5-Benzoyloxy-2 : 2 : 3 : 3-tetramethyl-Δ^4-*cyclo*pentenone with Palladium and Hydrogen* (IX).—When an acetic acid solution of the pure derivative, m. p. 68° (1·9 g.), was shaken with palladised barium sulphate (equivalent to 0·5 g. palladium) in an atmosphere of hydrogen at ordinary pressure, absorption ceased after 1 hour, 150 c.c. being taken up (calc. for 1 mol. of hydrogen, 160 c.c.). The mixture was poured into water, and an ethereal extract of the product was washed twice with ice-cold 5% sodium hydroxide solution and dried with calcium chloride. Evaporation yielded the reduction product as a rapidly crystallising oil. It separated from ligroin (b. p. 40—60°) in pearly plates, m. p. 60°. Identity was established by mixed melting points and by analysis (Found: C, 73·6; H, 8·0. Calc. for $C_{16}H_{20}O_3$: C, 73·8; H, 7·7%).

Reduction of 5-p-*Bromobenzyloxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^4-cyclo*pentenone* (XV).—The pure derivative (1·5 g.) in glacial acetic acid solution was shaken with palladised barium sulphate and hydrogen (pressure, 30 lb./sq. in.). Little absorption took place, and the bulk of the product was recovered unchanged. A substance, m. p. 26—27°, was isolated, but the quantity was insufficient for analysis.

Reduction of the Acetyl Derivative of 5-p-*Bromobenzyloxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^4-cyclo*pentenoneoxime* (XVI).—The acetoxime (1·0 g.) was reduced with 2½% sodium amalgam (100 g.) in acetic acid in the usual manner, and the basic portion of the product isolated and converted into the picrate of 5-hydroxy-2 : 2 : 3 : 3-tetramethyl-*cyclo*pentylamine, m. p. 210—215° (decomp.) (compare this vol., p. 403). The picrate was boiled for 2 hours under reflux with hydriodic acid (*d* 1·7) and red phosphorus, and the liquid was made alkaline and steam-distilled. The reduction product was isolated by extraction with ether and identified as 2 : 2 : 3 : 3-tetramethyl-*cyclo*pentylamine by conversion into the picrate.

Fission of Esters in Presence of Hydroxylamine.—Phenyl benzoate. The ester (2·0 g.), dissolved in absolute alcohol (20 c.c.), was treated with hydroxylamine hydrochloride (0·7 g.) and anhydrous sodium acetate (0·85 g.) on the steam-bath for 1 hour. The product was worked up into neutral, acid, and quasi-acid fractions: the latter two yielded benzoic acid and phenol respectively. The benzoic acid weighed 0·23 g., which is equivalent to 20% hydrolysis. A blank experiment in which the hydroxylamine hydrochloride was omitted yielded no trace of benzoic acid or phenol.

5-*Benzoyloxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanone* (X). The derivative (1·0 g.), hydroxylamine hydrochloride (1·0 g.), and anhydrous sodium acetate (1·2 g.), when similarly treated for 3 hours, gave an oily oxime (compare this vol., p. 1669) and practically pure benzoic acid (yield, 0·25 g.).

5-*Methoxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^4-cyclo*pentenone*. When the methoxy-compound was similarly treated with hydroxylamine hydrochloride (several mols.) and anhydrous sodium acetate for 3 hours, the product consisted mainly of a solid, together with a trace of oil. The solid was washed with ligroin and crystallised twice from boiling alcohol; it then had m. p. 210—211° (decomp.) (Found: C, 58·6, 58·7; H, 8·8, 8·7; N, 14·6, 14·6. Calc. for $C_9H_{16}O_2N_2$: C, 58·7; H, 8·7; N, 15·0%) and was identified as the dioxime of 3 : 3 : 4 : 4-tetramethyl*cyclo*pentan-1 : 2-dione by direct comparison and by mixed melting point.

Oxidation of 5-*Benzoyloxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^4-cyclo*pentenone* (IX).—(A) *With potassium ferricyanide.* The benzoyloxy-compound (1·0 g.) and anhydrous potassium carbonate (2·0 g.),

dissolved in dilute alcohol, were treated at 60° with potassium ferricyanide (9·3 g.) in alcoholic solution during 5 days, and the mixture was left for 5 days at the same temperature. The solution was acidified and the acid products were removed with ether: on evaporation a mixture of solid acids was obtained. After successive removals of benzoic acid, by solution in water, cooling to 0° and filtration, an acid was obtained which, after crystallisation from ethyl acetate–ligroin, had m. p. 140° and was identified as the lactonic acid of γγ-dihydroxy-ααββ-tetramethylglutaric acid by mixed melting point and by hydrolysis (Found: C, 53·2; H, 6·9. Calc. for $C_9H_{14}O_5$: C, 53·4; H, 6·9%).

(B) *With hydrogen peroxide.* The derivative (0·5 g.), dissolved in an aqueous acetone solution of sodium carbonate containing a trace of ferrous sulphate, was treated with 2·4 c.c. of 3% hydrogen peroxide at 0°. Benzoic acid was precipitated on acidification and removed by filtration. From the filtrate, an acid was obtained which, after two crystallisations from ethyl acetate–ligroin, had the characteristic form and m. p. (144°) of ααββ-tetramethylglutaric acid. The melting point of a mixture with a genuine specimen was 143—144°, but that of a mixture with the above lactonic acid was depressed to 115—120°.

Oxidation of 5-Acetoxy-2 : 2 : 3 : 3-tetramethyl-Δ^4-cyclopentenone (IV).—The pure acetoxy-compound was prepared from the hydroxy-ketone by treatment with acetyl chloride in pyridine solution. The pale yellow oil (0·5 g.) and anhydrous potassium carbonate (1·0 g.), dissolved in dilute alcohol, were treated with alcoholic potassium ferricyanide (5·0 g.), added during 3 days, and the mixture was left for 3 days at 45°. After extraction with ether, the liquid was acidified and again extracted with ether. This extract yielded a solid acid which, after crystallisation from ethyl acetate–ligroin, had m. p. 190° and was identified as tetramethylsuccinic acid. The yield was poor and the neutral ethereal extract gave some unchanged acetoxy-compound on evaporation.

Oxidation of 2 : 2 : 3 : 3-Tetramethyl-Δ^6-cyclopenten-5-ol-4-one (2 : 2 : 3 : 3-Tetramethyl-[0,1,2]-dicyclopentan-4-ol-5-one).—This was carried out with the quantities and by the procedure given above for the acetoxy-compound. A good yield of tetramethylsuccinic acid, m. p. 190° after crystallisation from ethyl acetate–ligroin, was obtained.

One of us (C. W. S.) wishes to record his indebtedness to the Royal Commission of 1851 for a Senior Studentship.

THE UNIVERSITY, LEEDS. [*Received, May 25th, 1928.*]

CCXLIII.—*Dichloro*-o-*xylenes.*

By LEONARD ERIC HINKEL, ERNEST EDWARD AYLING, and LILIAN COLLIER BEVAN.

WITH the exception of 3 : 5-dichloro-*o*-xylene (Crossley, J., 1902, **81**, 1536) there appears to be no trustworthy information concerning the dichloro-*o*-xylenes. The direct chlorination of *o*-xylene was considered by Claus and Kautz (*Ber.*, 1885, **18**, 1367) to yield only a liquid dichloro-derivative, b. p. 227° and solidifying at 3°, which Claus and Groneweg (*J. pr. Chem.*, 1891, **43**, 352) believed to be 4 : 5-dichloro-*o*-xylene. Koch, however, showed (*Ber.*, 1890, **23**, 2321) that the liquid was a mixture, which slowly deposited a dichloro-*o*-xylene, m. p. 73°. Villiger (*Ber.*, 1909, **42**, 3529), moreover, considered the dichlorophthalic anhydride obtained by Claus and Groneweg from the liquid derivative to be a mixture.

Ferrand (*Compt. rend.*, 1901, **133**, 169) claims to have identified three dichloro-derivatives from the chlorination. He regards the solid, m. p. 73°, as the 3 : 4-dichloro-*o*-xylene and the two liquids, b. p. 226—228° and 229·5—231·5°, as mixtures of the 4 : 5- and 3 : 6-dichloro-derivatives; little reliance, however, can be placed on his work, since he employed *o*-xylene containing as much as 10% of *m*-xylene. From the solid, he obtained a dichlorophthalic anhydride, m. p. 186°, corresponding to the 4 : 5- and not the 3 : 4-dichloro-anhydride as he supposed (compare Villiger, *loc. cit.*).

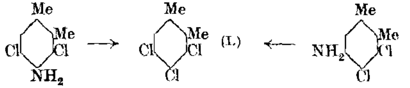
The chlorination of pure *o*-xylene under conditions designed to produce dichloro-derivatives has been studied with the result that all the dichloro-*o*-xylenes can now be described. The only one about which any doubt exists is 3 : 6-dichloro-*o*-xylene. It is produced in such small amount that it has not been possible thoroughly to investigate its properties, but it will be described more fully when experiments now in progress for its synthesis are completed.

The first action of chlorine on *o*-xylene results in the formation of *o*-3- and *o*-4-monochloro-derivatives in the proportion of 1 to 2 (Kruger, *Ber.*, 1885, **18**, 1755; Claus and Baeyer, *Annalen*, 1893, **274**, 304), and on further chlorination the former should yield the 3 : 4- and the 3 : 6- and the latter the 3 : 4- and the 4 : 5-dichloro-derivatives. Dichlorination, therefore, should yield principally 3 : 4- and 4 : 5-dichloro-*o*-xylenes together with a small quantity of 3 : 6-dichloro-*o*-xylene. This has been proved to be the case.

The dichloroxylene of m. p. 76° yields on oxidation a dichlorophthalic anhydride, m. p. 187°, and is therefore 4 : 5-*dichloro*-o-*xylene* (compare Villiger, *loc. cit.*). On nitration it yields 4 : 5-*dichloro*-3-*nitro*-o-*xylene*, reduction of which gives 4 : 5-*dichloro*-o-3-*xylidine*.

Diazotisation of the xylidine by the Gattermann process gave an altogether unforeseen result, tetrachloro-*o*-xylene being formed with the expected 3 : 4 : 5-trichloro-*o*-xylene. The former probably results from further chlorination occurring in the presence of the cuprous chloride and concentrated hydrochloric acid.

The liquid dichloro-*o*-xylene, b. p. 234°, on nitration gave as the main product a *mononitro*-derivative. Substitution of chlorine for the amino-group in the corresponding amine (m. p. 63°) gave 3 : 4 : 5-trichloro-*o*-xylene, m. p. 96° (I) (compare Hinkel, J., 1920, **117**, 1296). This trichloro-compound could theoretically be obtained from all the dichloro-*o*-xylenes except the 3 : 6-isomeride; consequently, since the constitution of the 4 : 5-isomeride has been established, the liquid compound must have the chlorine atoms either in the 3 : 4- or the 3 : 5-positions and the dichloro-*o*-xylidine, m. p. 63°, must therefore be represented by (II) or (III).

(II.)  (I.) (III.)

3 : 5-*Dichloro-o-4-xylidine* (II) has been synthesised by Crossley from *o*-4-acetoxylidide (J., 1904, **85**, 264) and has now been obtained more conveniently from 3 : 5-dichloro-*o*-xylene. The melting points of the amine so prepared and of its acetyl derivative have been raised to 47·5° and 196°, respectively. The amine of m. p. 63° must consequently be 5 : 6-*dichloro*-o-4-*xylidine* (III), and the liquid of b. p. 234° 3 : 4-*dichloro-o-xylene*. This orientation has been substantiated by the conversion of 3 : 4-dichloro-*o*-xylene into the corresponding *dichloro*-o-*diamine*, which gave the characteristic test for *o*-diamines with phenanthraquinone.

The constitutions of three out of the four possible dichloro-*o*-xylenes are thus definitely established and the fourth isomeride, m. p. 68°, must therefore be 3 : 6-*dichloro*-o-*xylene*. Reduction of its mononitro-derivative gave the corresponding xylidine. Replacement of the amino-group by chlorine in the usual manner gave, instead of 3 : 4 : 6-trichloro-*o*-xylene (compare Hinkel, *loc. cit.*), a mixture of chloro-compounds which, owing to the small quantity available, could not be further investigated.

The three dichloro-*o*-xylenes yield the same tetrachloro-*o*-xylene on further chlorination.

EXPERIMENTAL.

Chlorine was passed into pure *o*-xylene (b. p. 143·5°) at −10° in presence of iron filings until the gain in weight corresponded to

2 atoms of chlorine. After being washed with water and with sodium hydroxide solution, the liquid was dried and distilled; on boiling, a vigorous evolution of hydrogen chloride occurred due to the decomposition of intermediate additive compounds. Three main fractions were ultimately collected: (i) 225—230°; (ii) 230—236°; (iii) 236—246°.

Fraction (i), when cooled in ice, deposited 3 : 6-*dichloro*-o-*xylene*, which crystallised from methyl alcohol in white, iridescent flakes, m. p. 68°, b. p. 227° (corr.) (Found: Cl, 40·9. $C_8H_8Cl_2$ requires Cl, 40·6%).

Fraction (ii) gave 3 : 4-*dichloro*-o-*xylene*, b. p. 234° (corr.). This solidified when cooled in a mixture of ice and salt and melted at 9° (Found: Cl, 40·7%).

Fraction (iii), when cooled in ice, gave 4 : 5-*dichloro*-o-*xylene*, which crystallised from methyl alcohol in long, transparent needles, m. p. 76°, b. p. 240° (corr.) (Found: Cl, 40·6%).

Conversion of the Dichloro-o-*xylenes into Tetrachloro*-o-*xylene*.—Each of the dichloro-*o*-xylenes was chlorinated as described by Hinkel (J., 1920, **117**, 1300). Repeated crystallisation from alcohol or ethyl acetate of the tetrachloro-*o*-xylene so prepared does not entirely remove the last trace of any trichloro-*o*-xylene formed during the chlorination, but this can be readily achieved by crystallisation from carbon tetrachloride containing a small quantity of chloroform. The pure compound so obtained melts at 227°.

Oxidation of 4 : 5-*Dichloro*-o-*xylene*.—2 G. of 4 : 5-dichloro-*o*-xylene were heated with 15 c.c. of nitric acid (*d* 1·15) in a sealed tube for 7 hours at 180°. The resulting liquid was evaporated to dryness over solid caustic soda in a vacuum. The acid obtained melted at 199—200° after crystallisation from water. The anhydride, prepared by heating the acid with acetyl chloride, separated from carbon tetrachloride in small crystals, m. p. 187° (compare Villiger, *loc. cit.*).

4 : 5-*Dichloro*-3-*nitro*-o-*xylene*.—2 G. of 4 : 5-dichloro-*o*-xylene were added to 20 c.c. of a mixture of fuming nitric acid (3 vols.) and glacial acetic acid (1 vol.) and heated on a steam-bath for 7 minutes. The solution was poured into water; the solid which separated crystallised from alcohol in fine white needles, m. p. 117° (Found: Cl, 32·5. $C_8H_7O_2NCl_2$ requires Cl, 32·3%).

4 : 5-*Dichloro*-3 : 6-*dinitro*-o-*xylene*.—1 G. of 4 : 5-dichloro-*o*-xylene was heated for 10 minutes with 5 c.c. of sulphuric acid and 3 c.c. of nitric acid. The white solid that separated crystallised from alcohol in colourless prisms, m. p. 210° (Found: Cl, 26·65. $C_8H_6O_4N_2Cl_2$ requires Cl, 26·8 %).

4 : 5-*Dichloro*-o-3-*xylidine*.—A mixture of 3 g. of 4 : 5-dichloro-

3-nitro-*o*-xylene, 9 g. of iron filings, and 30 c.c. of glacial acetic acid was heated with frequent stirring for several hours on a steam-bath. The resulting solid was made alkaline and distilled with steam. The solid product crystallised from aqueous alcohol in long, silky needles, m. p. 88° (Found: Cl, 37·2. $C_8H_9NCl_2$ requires Cl, 37·3%). The *acetyl* derivative, prepared in the usual manner, crystallised from aqueous alcohol in small rosettes, m. p. 197° (Found: Cl, 30·8. $C_{10}H_{11}ONCl_2$ requires Cl, 30·6%).

Conversion of 4 : 5-*Dichloro*-o-3-*xylidine into* 3 : 4 : 5-*Trichloro*-o-*xylene*.—The amine, 0·5 g. at a time, was dissolved by heating in 10 c.c. of concentrated hydrochloric acid and 25 c.c. of water. The finely divided hydrochloride obtained on cooling was diazotised, and the whole was poured into a solution of cuprous chloride and distilled in steam. The solid obtained, after crystallising from methyl alcohol, softened at 95° and melted completely at 105°. It was obviously a mixture, although not consisting of 3 : 5 : 6- and 3 : 4 : 5-trichloro-*o*-xylenes, which melt at 47·5° and 96° respectively. Repeated fractional crystallisation from carbon tetrachloride containing varying amounts of chloroform resolved the mixture into 3 : 4 : 5-trichloro-*o*-xylene, m. p. 96°, and tetrachloro-*o*-xylene, m. p. 227°.

4 : 5-*Dichloro*-3 : 6-*diamino*-o-*xylene*.—4 : 5-Dichloro-3 : 6-dinitro-*o*-xylene was reduced in alcoholic solution by means of sodium hydrosulphite. After removal of the alcohol under reduced pressure, the solid was crystallised from alcohol, the *diamine* separating in small, white needles, m. p. 186°, decomp. 187° (Found: Cl, 34·4. $C_8H_{10}N_2Cl_2$ requires Cl, 34·6%).

3 : 4-*Dichloro*-5-*nitro*-o-*xylene*.—3 : 4-Dichloro-*o*-xylene was nitrated as described on p. 1876. The solid obtained was crystallised from alcohol, and separated from a small quantity of the 6-nitro-isomeride by washing with light petroleum (b. p. 40—60°) at 0°. It finally crystallised from light petroleum in clumps of hard, prismatic needles, m. p. 78° (Found: Cl, 32·0. $C_8H_7O_2NCl_2$ requires Cl, 32·3%).

3 : 4-*Dichloro*-5 : 6-*dinitro*-o-*xylene*.—3 : 4-Dichloro-*o*-xylene was nitrated as described on p. 1876. The resulting solid crystallised from ethyl acetate in prismatic needles, m. p. 172° (Found: Cl, 27·1. $C_8H_6O_4N_2Cl_2$ requires Cl, 26·8%).

5 : 6-*Dichloro*-o-4-*xylidine*.—3 : 4-Dichloro-5-nitro-*o*-xylene was reduced as described on p. 1876. The solid product crystallised from aqueous alcohol in a felt-like mass of white needles, m. p. 63° (Found: Cl, 37·1. $C_8H_9NCl_2$ requires Cl, 37·3%). The *acetyl* derivative crystallised from aqueous alcohol in fine needles, m. p. 147° (Found: Cl, 30·6. $C_{10}H_{11}ONCl_2$ requires Cl, 30·6%).

3 : 4-*Dichloro*-5 : 6-*diamino*-o-*xylene*.—3 : 4-Dichloro-5 : 6-dinitro-*o*-xylene was reduced with sodium hydrosulphite as described on p. 1877. The *diamine* obtained crystallised from aqueous alcohol in hair-like crystals, m. p. 176° (Found : Cl, 34·8. $C_8H_{10}N_2Cl_2$ requires Cl, 34·6%). The diamine and phenanthraquinone in acetic acid gave a *yellow precipitate*.

3 : 6-*Dichloro*-4-*nitro*-o-*xylene*.—3 : 6-Dichloro-*o*-xylene was nitrated under the conditions described on p. 1876. The solid obtained crystallised from methyl alcohol in small, white needles, m. p. 95° (Found : Cl, 32·2. $C_8H_7O_2NCl_2$ requires Cl, 32·3%).

3 : 6-*Dichloro*-4 : 5-*dinitro*-o-*xylene*, prepared from 3 : 6-dichloro-*o*-xylene by the method described on p. 1876, crystallised from alcohol in small, transparent, colourless prisms, m. p. 220° (Found : Cl, 26·4. $C_8H_6O_4N_2Cl_2$ requires Cl, 26·8%).

3 : 6-*Dichloro*-o-4-*xylidine*, obtained by reduction of 3 : 6-dichloro-4-nitro-*o*-xylene as described on p. 1876, crystallised from aqueous alcohol in white, silky needles, m. p. 82° (Found : Cl, 37·2. $C_8H_9NCl_2$ requires Cl, 37·3%). It could not be acetylated by the ordinary methods, but when it was heated for 1 hour on the water-bath with acetic anhydride–acetyl chloride the *diacetyl* derivative was obtained. This crystallised from alcohol in transparent prisms, m. p. 141° (Found : Cl, 25·8. $C_{12}H_{13}O_2NCl_2$ requires Cl, 25·9%).

3 : 5-*Dichloro*-4-*nitro*-o-*xylene*.—5 G. of 3 : 5-dichloro-*o*-xylene prepared according to Crossley (J., 1902, **81**, 1533) were heated for 30 minutes on a water-bath with 125 c.c. of a mixture of fuming nitric acid (3 vols.) and glacial acetic acid (1 vol.). The solid obtained by pouring the mixture into water crystallised from alcohol in a felt-like mass, m. p. 92°, which became waxy when pressed. It could not be freed from the small quantity of the 6-nitro-isomeride also formed during the nitration (Found : Cl, 32·1. $C_8H_7O_2NCl_2$ requires Cl, 32·3%).

3 : 5-*Dichloro*-o-4-*xylidine*.—The crude 3 : 5-dichloro-4-nitro-*o*-xylene (m. p. 92°) (5 g.) was reduced with iron filings and acetic acid as described on p. 1876. The solid produced was dissolved in alcohol; a few yellowish-white needles, m. p. 171°, then separated. The filtrate from these crystals (which were probably 3 : 5-dichloro-6-amino-*o*-xylene and were not further examined) was diluted slightly with water; the fine needles that separated crystallised from aqueous alcohol in small rosettes, m. p. 47·5°. The acetyl derivative, prepared in the usual manner, crystallised from boiling water in fine needles, m. p. 196° (Crossley gives m. p. 44·5° and 186°, respectively).

UNIVERSITY COLLEGE, SWANSEA. [*Received, April 14th*, 1928.]

CCXLIV.—*The Nitration of* m-*Fluorophenol.*

By Herbert Henry Hodgson and Joseph Nixon.

Although *m*-fluorophenol has been prepared (Swarts, *Bull. Acad. roy. Belg.*, 1913, 241), no mention of the nitro-derivatives appears in the literature. The present investigation proceeds on similar lines to those of the *m*-chloro- and *m*-bromo-analogues (J., 1925, **127**, 1599; 1926, 155). A trustworthy method for the preparation of *m*-fluoronitrobenzene from *m*-nitroaniline is described.

Monosulphonation of 3-fluoro-2-nitrophenol in the cold or at 100—120° appears to give exclusively 3-fluoro-2-nitrophenol-4-sulphonic acid, since only 3-fluoro-2 : 6-dinitrophenol could be obtained from it by further mononitration.

The orientations proposed for the dinitro-compounds follow from the modes of preparation and by analogy with the corresponding chloro- and bromo-compounds (*loc. cit.*). In addition is the following evidence: (1) All three dinitro-compounds are convertible into 3-fluoro-2 : 4 : 6-trinitrophenol, indicating that the two nitro-groups in each compound are in meta-positions to each other. (2) The 4 : 6-dinitro-compound gives 4 : 6-dinitro-*m*-phenylenediamine, and the 2 : 6- and 2 : 4-isomerides give the same 2 : 4-dinitro-*m*-phenylenediamine, when heated in a sealed tube with aqueous ammonia. (3) 3-Fluoro-2 : 4- and -2 : 6-dinitrophenols both give 2 : 4-dinitroresorcinol when boiled with aqueous sodium hydroxide.

Certain marked differences in behaviour of the fluoro- and the other halogeno-analogues have been observed: (*a*) 3-Fluoro-4 : 6-dinitrophenol forms a stable, yellow, crystalline silver derivative which does not exhibit transformations similar to those of the chloro-, bromo-, and iodo-compounds. The silver derivative of 3-fluoro-2 : 6-dinitrophenol, however, is produced initially as a yellow gel which rapidly passes through an orange-red gel stage into a permanent orange-red crystalline form. (*b*) The silver derivative of 3-fluoro-2 : 4-dinitrophenol has a deeper red colour than its 2 : 6-isomeride—the chloro- and bromo-analogues are yellow, crystalline substances. (*c*) All the silver derivatives are readily soluble in aqueous ammonia (compare the insolubility of the silver derivatives of the 3-halogeno-2 : 4 : 6-trinitrophenols and the varying solubility of the lower nitrated products). (*d*) The 3-fluoro-2-, -4-, and -6-nitrophenols resist acetylation. (*e*) Anomalies are exhibited in the m. p.'s: *e.g.*, 3-fluoro-4-nitrophenol has m. p. 56·5°, its analogues have m. p.'s 122°, 131°, and 124°; 3-fluoro-2 : 4 : 6-trinitrophenol has m. p. 173°, whereas the chloro-, bromo-, and iodo-compounds melt at 114°, 149°, and 197°, respectively.

EXPERIMENTAL.

Initial Materials.—A solution of *m*-nitroaniline (140 g.) in 60% hydrofluoric acid (450 c.c.) in a copper beaker was diazotised at 0° with a rapid stream of nitrous fumes (30 minutes) and added gradually to 60% hydrofluoric acid (75 c.c.), in a lead pot with a copper reflux condenser, heated on a boiling water-bath. The mixture was kept hot for 1 hour and the *m*-fluoronitrobenzene then isolated, in 25% yield, by steam-distillation. It was reduced to *m*-fluoroaniline, which was converted in almost quantitative yield into *m*-fluorophenol (Hodgson, E.P. 200,714).

Nitration.—The methods of preparation of the 3-fluoronitrophenols are those described for the corresponding chloro- and bromo-analogues with appropriate modifications.

3-Fluoro-6-nitrophenol (yield, 6 g. from 29 g. of *m*-fluorophenol) i: volatile in steam and crystallises from light petroleum in yellov needles, m. p. 32°, having a characteristic sweet nitrophenolic odou (Found: N, 9·1. $C_6H_4O_3NF$ requires N, 8·9%). The *sodium* sal crystallises from water in red needles. The orange-brown *silve* salt, which deepens in colour on keeping, is readily soluble in aqueou ammonia and gradually decomposes in boiling aqueous solutior The *methyl ether* crystallises from light petroleum in colourle: micro-parallelepipeds, m. p. 52° (Found: N, 8·3. $C_7H_6O_3N$ requires N, 8·2%), and the *benzoate* in colourless micro-scales, m.] 110—111° (Found: N, 5·6. $C_{13}H_8O_4NF$ requires N, 5·4%). Tl acetates of this substance and of its isomerides could not be prepare by any of the usual methods.

3-Fluoro-4-nitrophenol (yield, 9 g.) is non-volatile in steam ar crystallises from water or light petroleum in long, colourless needle m. p. 42° (Found: N, 9·2%). The *sodium* salt crystallises fro water in long, pale yellow needles. The bright yellow *silver* sa although more soluble in water and aqueous ammonia than i isomerides, also decomposes on boiling (Found: Ag, 40· $C_6H_3O_3NFAg$ requires Ag, 40·9%). The *methyl ether* crystallis from light petroleum in colourless needles, m. p. 56·5° (Foun N, 8·3%), and the *benzoate* in colourless, rectangular micro-plat m. p. 118° (Found: N, 5·6%).

3-Fluoro-2-nitrophenol, prepared by the nitration of disulphonat *m*-fluorophenol (J., 1925, **127**, 1600), passes over on hydrolysis ir current of steam as a reddish oil which, after being frozen a pressed, crystallises from light petroleum in short red needles, m. 39° (Found: N, 9·0%). The formation of a hydrate could not detected (compare J., 1926, 156, 631). The reddish-brown *sodi* salt is exceedingly soluble in water, and the very deep reddish-bro *silver* salt is readily soluble in hot water, but gradually decompos

and in aqueous ammonia. The *methyl ether* crystallises from light petroleum in long, colourless needles, m. p. 43·5° (Found : N, 8·4%), and the *benzoate* in clusters of white needles, m. p. 114° (Found : N, 5·5%).

3-*Fluoro*-4 : 6-*dinitrophenol* was prepared from *m*-fluorophenol and from 3-fluoro-6- and -4-nitrophenols in the same way as the corresponding bromo-compound (*loc. cit.*, p. 158). It is readily volatile in steam and crystallises from water or light petroleum in colourless needles, m. p. 80° (Found : N, 14·1. $C_6H_3O_5N_2F$ requires N, 13·9%).

In each preparation a non-volatile product was 3-fluoro-2 : 4 : 6 trinitrophenol. The silver salt, prepared like its analogues (*locc. cit.*, pp. 1603, 159, 634), separates very gradually in long, fine yellow needles and does not exhibit the phenomena recorded for the other three analogues. It is soluble in aqueous ammonia and stable in hot water (Found : Ag, 34·6. $C_6H_2O_5N_2FAg$ requires Ag, 34·9%).

3-*Fluoro*-2 : 6-*dinitrophenol* was prepared by recorded methods (*locc. cit.*, pp. 1602, 159) from 3-fluoro-2- and -6-nitrophenols. It crystallises from light petroleum in colourless needles, m. p. 68·5° (Found : N, 14·05%). The *silver* salt is readily soluble in aqueous ammonia and hot water, giving deep yellow solutions; from the aqueous solution, on cooling, it separates in orange-red microneedles (Found : Ag, 34·7%).

3-*Fluoro*-2 : 4-*dinitrophenol* was obtained together with 3-fluoro-2 : 6-dinitrophenol when *m*-fluorophenol was disulphonated and then dinitrated as in the procedure for the chloro-analogue (*loc. cit.*, p. 1602). The product was hydrolysed in a current of steam, the long, colourless needles of 3-fluoro-2 : 6-dinitrophenol which separated from the distillate on cooling were removed, and the filtrate was rendered alkaline and concentrated to a small bulk; on acidification, 3-*fluoro*-2 : 4-*dinitrophenol* was precipitated. It crystallised from light petroleum in pale yellow micro-parallelepipeds, m. p. 138—139° (Found : N, 13·9%), and was much more soluble in water than the other two isomerides. The deep red *silver* salt (Found : Ag, 34·6%) is readily soluble in hot water and aqueous ammonia, giving deep yellow solutions.

Action of Ammonia on 3-*Fluoro*-4 : 6-, -2 : 6-, *and* -2 : 4-*dinitrophenols*.—These (0·5 g.) were separately heated in sealed tubes with concentrated ammonia (5 c.c.) at 150° during 2 hours. On cooling, the products were obtained as brownish-yellow needles. The 4 : 6-dinitro-*m*-phenylenediamine obtained from the first-named compound melted at about 300° (compare Nietzki and Schedler, *Ber.*, 1897, **30**, 1667) (Found : N, 28·5. Calc. : N, 28·3%). 3-Fluoro-2 : 6- and -2 : 4-dinitrophenols each gave 2 : 4-dinitro-*m*-phenylenediamine, m. p. and mixed m. p. 264° (Barr, *Ber.*, 1888,

21, 5545, *gives m. p. 250°*; Hodgson and Moore, *loc. cit.*, give m. p. 258°) (*Found* : N, 28·4% and 28·2%, respectively).

The two specimens of 2 : 4-dinitroresorcinol obtained from 3-fluoro-2 : 6- and -2 : 4-dinitrophenols by the action of boiling aqueous sodium hydroxide melted, alone or mixed with each other, at 146° (compare *loc. cit.*, p. 160).

3-*Fluoro*-2 : 4 : 6-*trinitrophenol* crystallises from water in characteristic, almost colourless, hexagonal plates, m. p. 173° (Found : N, 17·1. $C_6H_2O_7N_3F$ requires N, 17·0%), which are not volatile in steam but sublime slowly from boiling concentrated sulphuric acid. This property is exhibited also by the other halogeno-analogues. The substance does not possess the violent sternutatory properties of the iodo-analogue, forms deep yellow solutions in water and alcohol, and is not brominated when its aqueous solution is treated with bromine. The bright yellow crystalline *silver* salt is readily soluble in aqueous ammonia and hot water.

The authors' thanks are due to the British Dyestuffs Corporation for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, April 27th, 1928.*]

CCXLV.—*Studies in Colour and Constitution. Part III. The Influence of the Methylthiol, Methoxy-, and Chlorine Groups on the Colours of the Nitrobenzaldehydephenylhydrazones.*

By HERBERT HENRY HODGSON and FREDERICK WILLIAM HANDLEY.

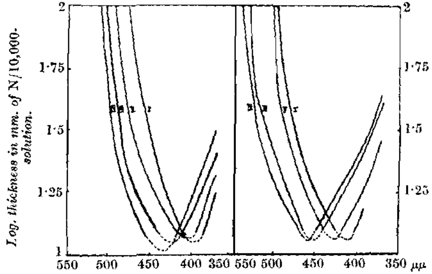
THE study of the influence of the methylthiol, methoxy-, and chlorine groups on the colours of simple azo-dyes (this vol., p. 162) has been extended to certain nitrobenzaldehydephenylhydrazones containing these substituents in ortho- and para-positions in the benzaldehyde and phenylhydrazine residues, respectively. In addition to the visual observations, absorption spectra data are included; work in the latter field has been recorded by Baly and Tuck (J., 1906, **89**, 982), Hewitt, Johnson, and Pope (J., 1914, **105**, 364), and Ciusa and Rastelli (*Atti R. Accad. Lincei*, 1919, **28**, ii, 366; 1920, **29**, ii, 146; *Gazzetta*, 1922, **52**, ii, 121, 126).

Trustworthy conclusions could not be deduced from the colours of the solid hydrazones because of their wide variation with the mode of crystallisation, but equimolecular alcoholic solutions exhibited a well-defined order. The absorption spectra curves of the *p*-nitrobenzaldehydephenylhydrazones confirm the results of the visual observations, and the relative order of the effects of the substituents

is the same whether these are present in the aldehyde or the hydrazine residue and is independent of the position of the nitro-group, *viz.*,

o-Cl, *o*-SMe, *p*-Cl, H, *o*-OMe, *p*-SMe, *p*-OMe.
Lemon-yellow ⟶ Increasing depth ⟶ Deep reddish-orange

The influence of the substituents is, in general, less marked than in the case of the azo-dyes; *e.g.*, (1) *o*-methoxyl is much less bathochromic; (2) *p*-methoxyl, which is only slightly bathochromic in the dyes, has a strong effect in the hydrazones, equalling or even exceeding that of *p*-methylthiol; (3) the feeble hypsochromic effect of *o*-chlorine in the dyes becomes most pronouncedly so in the hydrazones.



	Centre of band.		Centre of band.
I p-*Nitrobenzaldehyde*-o-*chlorophenylhydrazone*	395	I p-*Nitrobenzaldehyde*-p-*chlorophenylhydrazone*	413
II p-*Nitrobenzaldehyde*-o-*methylthiolphenylhydrazone*	405	II p-*Nitrobenzaldehydephenylhydrazone*	425
III p-*Nitrobenzaldehydephenylhydrazone*	425	III p-*Nitrobenzaldehyde*-p-*methylthiolphenylhydrazone*	455
IV p-*Nitrobenzaldehyde*-o-*methoxyphenylhydrazone*	433	IV p-*Nitrobenzaldehyde*-p-*methoxyphenylhydrazone*	465

The colours of the solutions in alcoholic potash of all the hydrazones studied were in accord with the generalisations of Chattaway and Clemo (J., 1923, **123**, 3041); as, however, the same marked differences in colour did not occur, no further conclusions have been drawn therefrom.

The Chromoisomerism of p-*Nitrobenzaldehydephenylhydrazone.*—Ciusa and Vecciotti (*Atti R. Accad. Lincei*, 1911, **20**, i, 803) recorded the existence of two polymorphic forms of *p*-nitrobenzaldehydephenylhydrazone, and the following related phenomena have now been observed: (1) The hydrazone crystallises from glacial acetic

acid in yellow needles, m. p. 194°, which slowly become pale orange without alteration of m. p. (2) Exposure to ultra-violet light for some hours or to sunlight for some weeks failed to bring about any such change as that noted by Chattaway (*J.*, 1906, **89**, 462) for benzaldehydephenylhydrazone. (3) Addition of water to a solution of *p*-nitrobenzaldehydephenylhydrazone in glacial acetic acid precipitated a yellow variety which changed in a few seconds into the red form of Ciusa and Vecciotti, a transformation which occurs in the absence of sunlight.

Attempts to prepare *o*-methylthiolbenzaldehyde were unsuccessful.

EXPERIMENTAL.

4-*Methylthiolphenylhydrazine*, which could not be prepared satisfactorily by the methods of Hodgson and Beard (*J. Soc. Chem. Ind.*, 1926, **45**, 56T) and Thompson (*J. Soc. Dyers and Col.*, 1921, **31**, 7), was obtained as follows: The diazonium compound obtained from 4-thioanisidine hydrochloride (8 g.), concentrated hydrochloric acid (40 c.c.), and 20% aqueous sodium nitrite (18 c.c.) at 0° was reduced at 0° with stannous chloride (24 g.) and hydrochloric acid (24 c.c.), and the *hydrochloride* produced was collected after 1 hour, washed with a little concentrated hydrochloric acid, and recrystallised from hot water, separating in colourless, glistening plates (Found: N, 15·0; Cl, 18·45. $C_7H_{10}N_2S,HCl$ requires N, 14·8; Cl, 18·6%).

4-*Methylthiolphenylhydrazine*, liberated from a hot aqueous solution of the hydrochloride by alkali or sodium acetate, crystallised from water in colourless plates, m. p. 60° (Found: S, 20·8. $C_7H_{10}N_2S$ requires S, 20·65%).

2-*Methylthiolphenylhydrazine*.—The reaction product obtained by the above method from 2-thioanisidine hydrochloride consisted of a mixture of a pale brown, amorphous substance A (1·1 g.) and a colourless, crystalline substance B (7 g.). A melted below 100°, was insoluble in cold and decomposed by boiling water, and was probably analogous to certain compounds described by Thompson (*loc. cit.*), who suggested a diazo-hydrazide structure for them (compare Bamberger, *Ber.*, 1895, **28**, 840); it has not been studied further. B contained tin, which was removed from an aqueous solution of the substance by hydrogen sulphide; addition of alkali or sodium acetate then gave 2-*methylthiolhydrazine*, which crystallised from water in colourless needles, m. p. 40° (Found: S, 20·6. $C_7H_{10}N_2S$ requires S, 20·65%). Both 2- and 4-methylthiolphenylhydrazine reduce Fehling's solution and ammoniacal silver nitrate in the cold, and decompose on keeping.

4-Methylthiolbenzaldehyde (phenylhydrazone, m. p. 138°) was obtained by Friedländer and Lenk's method (*Ber.*, 1912, **45**, 2084).

Preparation of the Hydrazones.—A mixture of the aldehyde in glacial acetic acid and of a slight excess of the hydrazine hydrochloride in aqueous solution was warmed gently for 5 minutes. The hydrazone separated on cooling and was recrystallised from dilute acetic acid.

Comparison of the Colours of 0·001N-Alcoholic Solutions.

Aldehyde.	Substituents in the hydrazine.
	Order of increasing redness ⟶
o-Nitrobenzaldehyde.	*o*-Cl, *o*-SMe, *p*-Cl, H, *o*-OMe, *p*-SMe, *p*-OMe
	Lemon-yellow ←—orange—deep orange——→red orange
m-Nitrobenzaldehyde.	Pale yellow←——yellow——→ ←——orange——→
p-Nitrobenzaldehyde.	Yellow←—orange————reddish-orange——→

Hydrazine.	Substituents in the benzaldehyde.
o-Nitrophenylhydrazine.	*o*-Cl, *p*-Cl, H, *o*-OMe, *p*-SMe, *p*-OMe
	←Yellow————→ ←orange ←reddish-orange——→
m-Nitrophenylhydrazine.	←Yellow————→ ←orange——deep orange——→
p-Nitrophenylhydrazine.	←Yellow————→ ←orange——reddish-orange→

Colours with Alcoholic Potash.—A concentrated alcoholic solution of potassium hydroxide was added to a portion of each of the above solutions until no further change in colour occurred. The final colour is recorded below after the m. p. and is followed by the change on heating.

o-*Chlorobenzaldehyde*-o-*nitrophenylhydrazone*, orange needles, m. p. 178° (Found : Cl, 12·7. $C_{13}H_{10}O_2N_3Cl$ requires Cl, 12·9%). Deep blue. Unchanged.

p-*Chlorobenzaldehyde*-o-*nitrophenylhydrazone*, scarlet needles, m. p. 203—204° (Found : Cl, 12·9%). Blue. Unchanged.

o-*Methoxybenzaldehyde*-o-*nitrophenylhydrazone*, bright red needles, m. p. 176—177° (Found : N, 15·7. $C_{14}H_{13}O_3N_3$ requires N, 15·5%). Violet-blue. Unchanged.

p-*Methoxybenzaldehyde*-o-*nitrophenylhydrazone*, scarlet needles, m. p. 204° (Found : N, 15·8%). Blue-violet. Unchanged.

p-*Methylthiolbenzaldehyde*-o-*nitrophenylhydrazone*, scarlet needles, m. p. 225—226° (Found : S, 11·3. $C_{14}H_{13}O_2N_3S$ requires S, 11·1%). Blue-violet. Unchanged.

o-*Chlorobenzaldehyde*-m-*nitrophenylhydrazone*, pale orange needles, m. p. 171° (Found : Cl, 12·8%). Brownish-yellow. Deeper.

p-*Chlorobenzaldehyde*-m-*nitrophenylhydrazone*, orange-red plates, m. p. 172° (Found : Cl, 12·6%). Brownish-yellow. Deeper.

o-*Methoxybenzaldehyde*-m-*nitrophenylhydrazone*, reddish-orange plates, m. p. 176° (Found : N, 15·8%). Orange. Brownish-orange.

p-*Methoxybenzaldehyde*-m-*nitrophenylhydrazone*, orange-yellow plates, m. p. 156° (Found : N, 15·6%). Brownish-yellow. Deeper.

p-*Methylthiolbenzaldehyde*-m-*nitrophenylhydrazone*, old-gold prisms, m. p. 146° (Found: S, 11·4%). Brownish-yellow. Deeper.

p-*Chlorobenzaldehyde*-p-*nitrophenylhydrazone*, deep orange spears, m. p. 224° (Found: Cl, 12·7%). Violet. Deeper.

o-*Methoxybenzaldehyde*-p-*nitrophenylhydrazone*, brick-red needles, m. p. 204—205° (Found: N, 15·3%). Violet. Deeper.

p-*Methylthiolbenzaldehyde*-p-*nitrophenylhydrazone*, deep orange needles, m. p. 183° but turns yellow at 140—145° (Found: S, 11·3%). Violet. Deeper.

o-*Nitrobenzaldehyde*-o-*methylthiolphenylhydrazone*, deep orange needles, m. p. 87—88° (Found: S, 10·8%). Yellowish-green. Olive-green.

o-*Nitrobenzaldehyde*-p-*methylthiolphenylhydrazone*, brownish-red prisms, m. p. 204° (Found: S, 11·3%). Olive-green. Bluer.

m-*Nitrobenzaldehyde*-o-*methylthiolphenylhydrazone*, orange prisms, m. p. 118° (Found: S, 11·5%). Yellow. Brownish-yellow.

m-*Nitrobenzaldehyde*-p-*methylthiolphenylhydrazone*, orange-red plates, m. p. 152° (Found: S, 11·4%). Brown. Deeper.

p-*Nitrobenzaldehyde*-o-*methylthiolphenylhydrazone*, red needles, m. p. 147° (Found: S, 10·9%). Olive-green. Bluish-green.

p-*Nitrobenzaldehyde*-p-*methylthiolphenylhydrazone*, scarlet plates, m. p. 179° (Found: S, 11·3%). Olive-green. Bluish-green.

Benzaldehyde-p-*methylthiolphenylhydrazone*, colourless plates, m. p. 93° (Found: S, 13·5. $C_{14}H_{14}N_2S$ *requires* S, 13·2%). Yellow. Deeper.

p-*Methylthiolbenzaldehydephenylhydrazone*, m. p. 138° (Found: S, 13·4%). Yellow. Deeper.

Absorption Spectra.—These were obtained by means of a glass spectrograph, the source of light being an iron arc, and are shown in the figure.

The authors desire to thank Dr. H. Lowery for advice with respect to the absorption spectra, and the British Dyestuffs Corporation for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, May 9th*, 1928.]

CCXLVI.—*The Influence of Intensive Drying on the System Nitrogen Peroxide–Nitric Oxide–Oxygen.*

By JOHN WILLIAM SMITH.

IT was observed by Baker (J., 1894, **65**, 611) that when carefully purified gaseous nitric oxide and oxygen, which had been dried separately over phosphoric oxide for 10 days, were mixed, no

combination occurred, and on opening the container under dry mercury no contraction in volume was noted. When a trace of moisture was introduced, however, combination immediately took place. Hasche (*J. Amer. Chem. Soc.*, 1926, **48**, 2253) found that the velocity of reaction between carefully dried nitric oxide and oxygen was reduced by 20% if the walls of the reaction vessel were coated with paraffin wax. This he ascribed to a protective action, preventing the gases from coming into contact with the walls of the vessel, which would hold adsorbed water vapour. Briner (*J. Chim. physique*, 1926, **23**, 848) unsuccessfully attempted to repeat Baker's observations: although the duration of the drying in each case ranged from 3 months to a year, in no case did the gases remain colourless on mixing.

The thermal dissociation of nitrogen peroxide into nitric oxide and oxygen has been fairly fully worked out, notably by Richardson (J., 1887, **51**, 397), Bodenstein and Katayama (*Z. physikal. Chem.*, 1909, **69**, 44), and Bodenstein, Boes, Lindner, and Ramstetter (*ibid.*, 1922, **100**, 68). At pressures of the order of 1 atmosphere, considerable dissociation occurs at 500—600°. Hence it was thought that, if nitrogen peroxide were heated in the intensively dried state, interesting phenomena might be observed. Three possibilities presented themselves: (*a*) The nitrogen peroxide might not dissociate, *i.e.*, the colour of the gas would not diminish on strong heating. (*b*) Complete dissociation might occur into nitric oxide and oxygen, which might not recombine on cooling. (*c*) Some intermediate stage might be attained, and a definite shift in the chemical equilibrium might be observed, corresponding to a shift in the inner equilibrium in the case of dried liquids.

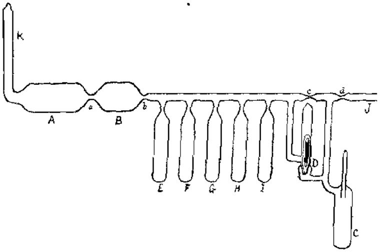
EXPERIMENTAL.

Apparatus No. 1.—The first apparatus employed was an adapted form of that used by Lewis and Rideal in their work on the synthesis of hydrogen bromide and the dissociation of hydrogen iodide (*J. Amer. Chem. Soc.*, 1926, **48**, 2554). The whole was constructed of "Durosil" glass which had been freed from capillaries by the method recommended by Smits and his co-workers (J., 1926, 2657). The apparatus (Fig. 1) consisted essentially of a horizontal tube carrying a series of reaction bulbs, *E*, *F*, *G*, *H*, *I*, each of which was connected to the horizontal tube through a capillary neck suitable for vacuum sealing. This tube connected at one end to two bulbs, *B* and *A*, for use when charging with phosphoric oxide, as described below, and at the other end to the vacuum pump system and to a bulb to serve as a nitrogen peroxide reservoir, connected as shown in the diagram.

After being cleaned with chromic acid, washed thoroughly, and dried roughly by heating to 300° in an electric oven, the apparatus was assembled and connected to a high-vacuum pump system through the tube *J*. After being tested for leakage, the whole apparatus was heated at 300° for 2 days, a high vacuum (10^{-6} mm.) being maintained in it during this period.

Dry air was then admitted, and pure resublimed phosphoric oxide introduced into *A* through *K*, which was immediately sealed off. The apparatus was again evacuated, all the tubes except bulb *A* being heated to 300°. It was then allowed to cool and bulb *A* was heated. In this way the pentoxide was sublimed in a vacuum from bulb *A* to bulb *B*. Bulb *A* was then removed by sealing off at

FIG. 1.



the constriction *a*. The reaction bulbs were heated strongly again, and, after cooling, the pentoxide was sublimed into them by heating the bulb *B*. The bulb *I* was kept free from the pentoxide, so as to serve as a standard of comparison, and a free space was left in each of the other bulbs to admit of colour observation being made through the tube. Each had been drawn from a tube of uniform diameter, so that rough quantitative colour comparison could be carried out. The bulb *B* was then drawn off at the constriction *b*, and constriction *c* was also sealed. This disconnected the bulbs from the vacuum pump system and from the reservoir bulb *D*. Dry air was then admitted to *C*, followed by a little phosphoric oxide and a few c.c. of dry nitrogen tetroxide. The tetroxide was frozen in liquid air and the bulb was evacuated again. Occluded air was removed by allowing the tetroxide to re-melt in a vacuum, after which it was frozen again and the bulb re-evacuated. When a high vacuum was reached, the whole apparatus was sealed off at the constriction *d*.

After being left for a few days to allow the nitrogen peroxide to dry, the bulb *C* was cooled in ice, and the septum *D* broken. The gas was allowed to reach equilibrium with the liquid at 0°, and the separate bulbs were sealed off. Thus these bulbs were all sealed off at the same known pressure, *viz.*, the vapour pressure of nitrogen peroxide at 0°—264 mm. The bulbs were matched on a tintometer to a Lovibond scale.

After the gas had been allowed to dry in the bulbs for a further 3 days, one of the bulbs was heated at 250—300° for 1½ hours. On cooling, the colour of the gas had diminished to about one-half of its original intensity, and after a further 5 hours' heating it became practically colourless. At the same time the phosphoric oxide changed completely in appearance, passing from a finely crystalline, snow-like mass into colourless transparent plates of a type that had not been observed previously under any conditions. None of the other bulbs became so nearly colourless, but in each case a very marked diminution in the intensity was observed.

The fact that the gas became so nearly colourless was at first thought to be due to an almost complete shift of the equilibrium towards the dissociated side. At this stage, however, I was privileged to see a private communication from Dr. Hartung to Professor Donnan, in which it was noted that nitrogen tetroxide reacted with phosphoric oxide at temperatures above 200°, yielding an addition compound. The formation of this compound appeared to account for the great diminution in the colour of the bulbs, so, as other lines of attacking the problem were being commenced, this investigation was abandoned.

Some months later, however, a rough analysis of the residual gas was carried out by breaking the tip of a bulb under pure, dry, recently boiled mercury. In tube 1 the colour intensity was about one-quarter of the initial intensity. On opening, the volume of residual gas was 4·43 c.c. The mercury, however, rose steadily, and after 24 hours the volume was 2·26 c.c. An attempt was then made to introduce a small drop of water into the tube, but the mercury only was moistened. An immediate further contraction in volume was observed. This was complete in 5 minutes, a further 24 hours' standing causing no further change. The residual gas was then mainly nitric oxide, for on introduction of a drop of ferrous sulphate solution a brown colour was produced. A small bubble of other gas of unknown composition remained, however. The total volume of the tube was 13·04 c.c., so the pressure of the gas remaining after heating was 238 mm. The bulb had been filled at a pressure of 264 mm., so it was concluded that some combination must have taken place with the phosphoric oxide, but that the pressure change was

small compared with the colour change. Hence it was concluded that the colour change was not due entirely to a simple absorption of the gas by the pentoxide.

This was confirmed by tube 2, in which the colour was too faint to match on the tintometer. The tip of this bulb was opened under mercury which had been carefully purified and dried over phosphoric oxide for a year. On the introduction of moisture, the residual gas immediately turned dark brown and contracted in volume from 3·02 c.c. to 1·30 c.c. The peroxide formed gradually acted on the mercury, leaving a bubble of nitric oxide at the top of the tube. The residual gas pressure (130 mm.) was here again large compared with that to be expected from the colour change.

Hence it seems quite clear that the tubes contained nitric oxide and oxygen, and that the moisture introduced caused recombination. The actual temperature of drying is here unknown—it may have been carried out before the tube was heated, or at the higher temperature when the gas was somewhat dissociated. At first sight, this result seems to be in conflict with that obtained later with apparatus No. 3, but it may be accounted for if the drying were effected while the gas was slightly dissociated. However, the residual gas appears to have been much more dissociated than normal nitrogen peroxide would be on heating to the same temperature under the same pressure, so a definite shift in the equilibrium seems to be indicated. These experiments seem to confirm Baker's observation of the co-existence of nitric oxide and oxygen gases in the intensively dried state.

Apparatus No. 2.—It was thought desirable to be able to test the residual gas in the absence of the nitrogen peroxide–phosphoric oxide compound, since it might be alleged that admission of moisture to the tubes liberated the peroxide from this compound, thereby causing the dark brown coloration. Such an explanation was regarded as very improbable, for the moisture was introduced only on the surface of the mercury and no gas was seen to rise from the compound, which was covered with mercury. This explanation, also, did not account for the rapid volume change. In this apparatus the bulbs were prepared with a constriction in the middle. Phosphoric oxide was sublimed into one section of this only, so that the compound could be removed before testing. The bulbs were sealed off at the same pressure as before.

Tube No. 6 was heated at 300° for 18 hours, the gas being then quite colourless. After cooling, the tube was divided, and the section free from the phosphoric oxide was opened under dry mercury. A considerable volume of gas remained. On the introduction of moisture, very little effect was noticed, however, and the

residual gas proved to be 2·81 c.c. of oxygen and 1·41 c.c. of nitrogen. No nitrous oxide could be found. The ratio of oxygen to nitrogen (2 : 1) is here so exact that it must be supposed that the peroxide had completely dissociated into its elements, although it does not normally do so at any appreciable rate at this temperature. The volume of the bulb was 22·17 c.c. The loss was presumably due to the compound formation. The bulb containing the compound was treated in exactly the same way, but no coloration was observed on introducing a little moisture, and no volume contraction occurred. Hence the results obtained with tubes 1 and 2 were shown not to be due to the decomposition of this compound. The introduction of excess of moisture caused only comparatively slow decomposition.

Tube 7 was heated at 300° for 6 hours. It was then cooled, divided, and opened under mercury as in the previous case. The mercury was not so dry as that used before, and the residual gas gradually contracted in volume and became deeper reddish-brown in colour. Rather more moisture than was desired was then added, and a definite aqueous film was produced. This caused a sharp contraction in volume which was complete in a very short time, further standing producing only a minute further contraction. The residual gas was again nitrogen and oxygen, but in about equal parts. The fact that the proportion of oxygen to nitrogen was lower in this case may be attributed to the interaction of some of the nitrogen peroxide with mercury, yielding nitric oxide, which absorbed more oxygen, and so on. This appears to confirm the observations made with tubes 1, 2, and 6.

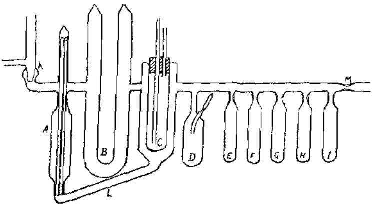
The decomposition of the nitric oxide into its elements may be catalysed by the large surface of the phosphoric oxide, which was very finely divided indeed. It has been found that the elements are not formed to any great extent on heating the nitrogen peroxide–phosphoric oxide addition compound, and also that they are not formed to any extent if the tubes are heated in the initial stages to temperatures of about 350°, at which the phosphoric oxide passes into the glass-like form. The evidence of these experiments shows that a temperature of about 300° and prolonged heating favour the decomposition of the nitrogen oxides into their elements, a reaction which is almost entirely absent at slightly lower temperatures.

The Effect of Intensive Drying at the Ordinary Temperature on the Thermal Dissociation of Nitrogen Peroxide into Nitric Oxide and Oxygen.—The apparatus employed (Fig. 2) embodied the circulation principle used by Smits, de Liefde, Swart, and Claassen (J., 1926, 2659). The liquid evaporated from the bulb *A*, passed through the phosphoric oxide in the wide U-tube *B*, and was condensed in *C*, which was cooled by a stream of water passing through the inner

tube, as shown. From here it ran back along the tube L into A. The apparatus was connected to a bulb, D, in which the liquid could be frozen out, and to a series of bulbs, E, F, G, etc., in which small amounts of the gas could be sealed off for testing purposes. The apparatus at this side ended in a connexion to a high-vacuum pump system through the constriction M. The constrictions joining the bulbs to the horizontal tube were not made very narrow, but the walls at these points were made very thick so that the bulbs could still be readily sealed off in a vacuum. This avoided the usual restriction on the diffusion of gases, and hence also of moisture, from the bulbs—a very serious drawback to capillaries in drying apparatus.

The whole apparatus was constructed of capillary-freed " Pyrex " glass. It was heated under a high vacuum for a week, after which phosphoric oxide was sublimed into the U-tube B. The nitrogen

FIG. 2.



peroxide was introduced into D, where it was frozen out, the apparatus was evacuated, and the constriction M sealed off. The apparatus was kept in an air thermostat at about 30° while a stream of cold water was passed through the inner vessel, C. In this way a steady circulation was maintained, the average amount condensing being about 10 drops a minute.

After 3 months, the liquid was all condensed in bulb D. This was then placed in a bath at 0°, and when equilibrium was reached a bulb of the gas was sealed off. The colour of the gas in this bulb, when matched on a tintometer, was not appreciably different from that of a blank undried specimen. The bulbs were slowly heated together in an electric furnace. The colours deepened similarly up to about 400°; on raising the temperature further, however, the colour of the undried gas appreciably lightened owing to dissociation into nitric oxide and oxygen, but that of the dried gas remained constant, so far as could be judged visually. The colour difference was quite

perceptible at 500°, and at 600° it was very marked. It being thought possible that the rate of dissociation was very much retarded by the intensive drying, the bulbs were maintained at 550° for 24 hours. Even after this period, the nitrogen peroxide did not appear to have dissociated to any appreciable extent. On slow cooling, the colour of the moist bulb became about the same as that of the dry bulb at about 400°. On further rather rapid cooling to room temperature, the dry bulb remained somewhat darker than the undried one. About 3 hours were required before the colour of the former returned to that of the moist bulb. This was evidently due to the slow rate of polymerisation of the NO_2 molecules.

From this simple experiment the following deductions may be drawn. (*a*) Intensively dried gaseous nitrogen peroxide does not dissociate very considerably into nitric oxide and oxygen, even on heating at 550° for 24 hours. (*b*) The rate of polymerisation of the coloured NO_2 molecules to form the colourless N_2O_4 molecules is retarded by the intensive drying.

After drying for 6 months, another bulb was sealed off from the same apparatus. The complication had now arisen that the vapour pressure at 0° had so far increased that the colour of the gas in equilibrium with the liquid at 0° was much darker than in the specimen "wet" tube. Accordingly, the liquid was cooled in a freezing mixture until the colours were as nearly matched as possible. The bulb was then sealed off. It was observed later that this bulb was a little lighter in colour than the standard tube. On heating to 600°, however, it was appreciably darker. The tubes were maintained at about 620° for 24 hours, this temperature being as near to the softening point of the glass as it was thought safe to heat the bulb. The bulbs were then of equal colour intensity, and on cooling and re-heating all abnormality seemed to have disappeared from the bulb. This was probably due to the fact that at such high temperatures the "Pyrex" glass tends to decompose superficially, evolving a small quantity of water.

Summary.

When nitrogen peroxide is heated with phosphoric oxide, at least three reactions take place: (*a*) The pentoxide combines with the nitrogen peroxide, yielding the compound described by Hartung (private communication). (*b*) The nitrogen peroxide is dissociated into nitric oxide and oxygen to a greater extent than in the moist gas, and these products do not recombine on cooling. (*c*) The nitric oxide decomposes into its elements at a greater rate than normally. This reaction may be catalysed by the large surface of the phosphoric oxide.

A temperature of about 300° and prolonged heating favour reaction (*c*).

Nitrogen peroxide which had been *intensively* dried at the ordinary temperature did not dissociate very considerably into nitric oxide and oxygen, even on heating at 550° for 24 hours, but on heating at about 620° for the same period, it seemed to revert completely to the normal form, probably owing to a superficial decomposition of the glass.

In the dried gas the rate of polymerisation of the coloured NO_2 molecules to form the colourless N_2O_4 molecules is retarded.

In conclusion, the author desires to express his thanks to the Department of Scientific and Industrial Research for a grant, and especially to Professor F. G. Donnan, F.R.S., for his helpful advice and criticism throughout the progress of this research.

The Sir William Ramsay Laboratories of Inorganic and Physical Chemistry, University College, London. [*Received, May 4th*, 1928.]

CCXLVII.—*The Thermal Decomposition of Thiobenzanilide.*

By Arthur William Chapman.

It is on record (Jacobson, *Ber.*, 1886, **19**, 1067) that thiobenzanilide decomposes when distilled, yielding hydrogen sulphide and 1-phenylbenzthiazole (I). As the thermal decomposition of the *S*-phenyl ether of thiobenzanilide (*N*-phenylbenziminophenyl thioether) had recently been investigated (*J.*, 1926, 2296), it appeared desirable to study the decomposition of the parent thiobenzanilide in greater detail, and, after a preliminary trial had confirmed the original statement that hydrogen sulphide and 1-phenylbenzthiazole were produced, experiments were carried out to determine if possible the precise mechanism of the change.

The simplest reaction by which 1-phenylbenzthiazole might be produced is the following :

$$C_{13}H_{11}NS = C_{13}H_9NS + H_2.$$

Experiment showed that hydrogen is not evolved in the decomposition, so if this reaction does take place, all the hydrogen is absorbed by some reducible material.

Under certain conditions, thioanilides are readily oxidised to thiazoles (compare Jacobson, *loc. cit.*) and the formation of thiazole in this case might be attributed to atmospheric oxidation. The

reaction, however, proceeds equally well in an atmosphere of an inert gas, so the oxygen of the air plays no part in the decomposition.

The hydrogen sulphide is not produced by direct reduction of the thioanilide thus,

$$\text{PhC(SH):NPh} \xrightarrow{2H} \text{PhCH:NPh} + H_2S,$$

since neither benzalaniline nor benzaldehyde was detected among the products of the reaction.

Separation of all the products of decomposition was attempted and *s*-diphenylbenzenylamidine (II) (yield, 11—19%), stilbene, and tetraphenylthiophen (III) were isolated in addition to hydrogen sulphide (37—40%) and 1-phenylbenzthiazole (38—58%). The quantities of stilbene and tetraphenylthiophen formed could not be determined.

The presence of the amidine indicated that aniline was present at some stage of the process. The yield was not affected by careful drying of the material before heating, and the formation of the amidine could therefore not be attributed to hydrolysis of the anilide. Aniline could, however, be formed by reduction of the thioanilide thus,

$$\text{Ph·CS·NHPh} \xrightarrow{2H} \text{Ph·CHS} + H_2N\text{·Ph},$$

the necessary hydrogen being furnished from the production of the thiazole. The thiobenzaldehyde would then decompose (compare Baumann and Klett, *Ber.*, 1891, **24**, 3307), yielding hydrogen sulphide, stilbene, and tetraphenylthiophen, all of which were actually isolated.

It appears very probable that this view of the decomposition is the correct one, as it is also in agreement with the yields of products isolated in the separations. The complete series of reactions can be represented by the scheme :

$$\text{Ph·CS·NHPh} \longrightarrow \text{(I) PhC}{<}{}^{N}_{S}{>}C_6H_4 + 2H.$$

$$2H + \text{Ph·CS·NHPh} \longrightarrow \text{Ph·NH}_2 + \text{Ph·CHS}.$$

$$\text{Ph·NH}_2 + \text{Ph·CS·NHPh} \longrightarrow \text{(II) PhC}{<}{}^{NPh}_{NHPh} + H_2S.$$

$$\text{Ph·CHS} \xrightarrow{heat} \text{CHPh:CHPh} + \text{(III)} {}^{\text{PhC:CPh}}_{\text{PhC:CPh}}{>}S + H_2S.$$

EXPERIMENTAL.

Numerous experiments were performed the results of which were all in agreement. Thiobenzanilide (5 g.) was placed in a large test-tube heated in an oil-bath and fitted with inlet and outlet tubes to enable the air to be replaced by carbon dioxide or nitrogen. The

exit tube was connected in series to a cooled U-tube, so that any volatile liquid product might be condensed and observed, and, in the experiments for the detection of hydrogen, to a nitrometer, or, in the other quantitative experiments, to a series of wash-bottles containing standard iodine solution to absorb hydrogen sulphide.

Decomposition occurred at 250° and brisk evolution of gas took place at 270° and above, the gaseous product being swept out by the current of nitrogen or carbon dioxide. The bath was maintained in different experiments at various temperatures between 250° and 310°. Above 270°, the decomposition was practically complete in an hour, but at 250° about half the material could be recovered unchanged at the end of that time.

The hydrogen sulphide formed was estimated by titration of the iodine solution in the absorption vessels. A trace of non-aqueous liquid, insufficient for examination, condensed in the connecting tube. It was probably aniline, as Jacobson detected a trace of aniline among the products obtained under his conditions. The residue in the tube was a very dark brown oil which crystallised on cooling. It was dissolved in ether, and the solution extracted repeatedly with dilute aqueous sodium hydroxide. The alkaline extract yielded unchanged thiobenzanilide on acidification. The ethereal solution was then evaporated, the residue extracted several times with hot concentrated hydrochloric acid, and the extract poured into five times its volume of water. A voluminous precipitate of 1-phenylbenzthiazole was produced which on crystallisation from alcohol gave colourless needles, m. p. 113—114°. When the aqueous acid filtrate was made alkaline with sodium hydroxide, *s*-diphenylbenzenylamidine was precipitated (long prisms, m. p. 145° after crystallisation from alcohol). The identity of every substance isolated in this investigation was confirmed by direct comparison and mixed melting-point determinations with an authentic specimen prepared by a known method.

The residue insoluble in hydrochloric acid was dark brown, oily above 100°, and hard and crystalline at room temperature. It represented about 20% of the weight of the original thiobenzanilide. After a number of attempted separations had indicated the nature of the material, the following method of purification was adopted, the residue from several batches of heated thiobenzanilide being used. Part of the material was submitted to steam-distillation; a small quantity of white solid distilled over, which on crystallisation from alcohol gave colourless scales, m. p. 114—121° (120° when mixed with stilbene). Further purification of this small specimen was not attempted. The remainder of the residue was distilled (b. p. 300° to above 400°), and the distillate crystallised from

alcohol. Slender needles of tetraphenylthiophen (m. p. 184—185°; very sparingly soluble in alcohol) were obtained. The mother-liquors were evaporated to dryness and the residue was taken up in carbon disulphide and treated with a slight excess of bromine. A precipitate of α-stilbene dibromide was immediately produced, which was purified by washing with absolute alcohol, in which it was very sparingly soluble (m. p. 237° decomp.).

The author wishes to express his indebtedness to the Chemical Society for a grant which has defrayed part of the cost of this investigation.

THE UNIVERSITY, SHEFFIELD. [*Received, May 12th, 1928.*]

CCXLVIII.—*The Action of Nitrous Acid on Amino-compounds. Part II. Aliphatic Amino-acids.*

By THOMAS WESTON JOHNS TAYLOR.

THE action of nitrous acid on aliphatic amino-acids is largely used for their estimation by the method of van Slyke (*J. Biol. Chem.*, 1911, **9**, 275; 1912, **12**, 275): a large excess of nitrous acid is employed, and the progress of the reaction followed by measuring the volume of nitrogen evolved. Apart from qualitative estimates of the relative speeds of reaction of various acids, however, no measurements of reaction velocity have been made, with the exception of the work of Dunn and Schmidt (*ibid.*, 1922, **53**, 401), who, using van Slyke's method, investigated a series of acids and showed that the reaction was more rapid the nearer the amino- and the carboxyl group were in the carbon chain. They also state that the amino-acid disappears at a rate in accordance with the unimolecular law, although their experimental results are far from consistent.

The amino-acids react with nitrous acid much more rapidly than do methylamine and ammonia, and in order to throw light on this difference, measurements of the reaction velocity in the cases of glycine, α-alanine, and β-alanine have been made. For reasons pointed out in Part I (this vol., p. 1099) any method similar to that of van Slyke is unsuitable, and the reaction has been followed by estimation of the amino-acid. It is shown that the difference referred to arises from the fact that, with an amino-acid $NH_2{\cdot}R{\cdot}CO{\cdot}OH$, the form $NH_3^+{\cdot}R{\cdot}CO{\cdot}O^-$ is able to react rapidly.

Method and Materials.—The reactions were investigated at 25° ± 0·1°. The solutions were made up from standard solutions of the amino-acid, of sulphuric acid and of pure barium nitrite; the mixture was protected by a layer of medicinal paraffin (see Part I),

through which passed a small stirrer and a tube; through the latter, samples were withdrawn from time to time by pipette.

The sample was immediately run into excess of aqueous baryta and the amino-acid content estimated by a modification of Sörensen's formaldehyde titration method (*Biochem. Z.*, 1908, **7**, 45). Phenolphthalein was added and dilute sulphuric acid run in from a burette until the pink colour just disappeared; excess of 20% formaldehyde solution, which had been previously neutralised to phenolphthalein by baryta, was then added and the amino-acid was titrated with 0·05*N*-baryta. The method was found by blank experiments to give results accurate to 1% in the case of glycine, if the final concentration of the glycine was not less than about 0·01*N*; with more dilute solutions the end-point is not very definite. In the case of the two aminopropionic acids the end-point is not so good and the accuracy consequently suffers; no other method giving a greater accuracy is, however, available.

The glycine was a commercial A.R. sample which had been recrystallised three times from aqueous alcohol. α-Alanine was prepared by the method of Zelinsky and Stadnikoff (*Ber.*, 1908, **41**, 2061) and β-alanine from succinimide (Holm, *Arch. Pharm.*, 1904, **242**, 597); after three recrystallisations from aqueous alcohol the α-compound melted at 295° (corr.) and the β at 206° (corr.); the latter melting point is 10° higher than that usually accepted, but agrees with the observation of Lengfeld and Stieglitz (*Amer. Chem. J.*, 1893, **15**, 508).

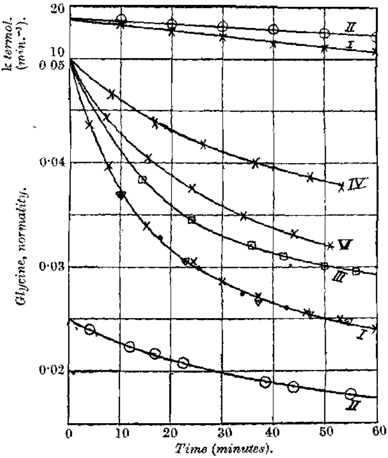
Results.

The three acids show qualitatively the same behaviour towards nitrous acid. At a dilution of 0·05*N* with an equivalent of barium nitrite no reaction could be detected over a period of 6 hours. With an equivalent of nitrous acid there is a rapid reaction unlike the cases of methylamine and ammonia; the rate of this reaction is lowered by the addition of mineral acids or of neutral salts.

Glycine.—Curves I and II of Fig. 1 show the rate of reaction with an equivalent of nitrous acid in 0·05*N*- and 0·025*N*-solution respectively. The reaction is so fast that nitrogen bubbles freely from the solution and thus the spontaneous decomposition of the nitrous acid is pronounced; consequently the interpretation of the results is not so simple as in the case of methylamine (Part I, *loc. cit.*). Since the velocity is lowered by the presence of sulphuric acid (Curves III and IV, Fig. 1) and since a product of the reaction is glycollic acid, experiments were carried out with solutions to which glycollic acid had been added (Curve I, Fig. 1). Even if this is in large excess (0·25*N*), however, the velocity of reaction is unaffected, and thus there is no negative autocatalysis.

The reaction with one equivalent of nitrous acid is approximately of the third order. From the smooth curves shown in Fig. 1 values of the glycine concentration at intervals of 10 minutes were read and from these termolecular velocity coefficients were calculated; these are shown in Table I for both 0·05*N*- and 0·025*N*-solutions; k cannot be expected to remain constant because of the marked

FIG. 1.



I. × 0·05N-*Glycine* + 0·05*N*-HNO_2.
• „ + „ + 0·05N-*glycollic acid.*
▽ „ + „ + 0·25N- „
II. 0·025N-*Glycine* + 0·025*N*-HNO_2.
III. 0·05N-*Glycine* + 0·05*N*-HNO_2 + 0·05*N*-H_2SO_4.
IV. „ + „ + 0·1*N*- „
V. „ + „ + 1·0*N*-KCl.

spontaneous decomposition of one of the reactants. If, however, these values are plotted against time, as in the upper part of Fig. 1, and straight lines are drawn through them, the lines for the two dilutions converge to the same value at time 0.

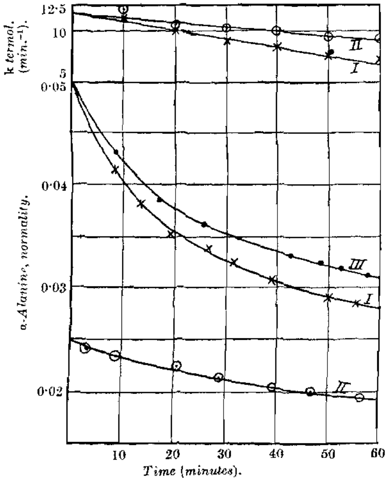
The values of k fall more rapidly for the stronger solution, as would be expected, since the rate of spontaneous decomposition of the nitrous acid is greater in that solution because of the higher rate

Table I.

Glycine.

min.	0·05*N*-Soln. *x* norm.	0·05*N*-Soln. *k* termol. (min.$^{-1}$).	0·025*N*-Soln. *x* norm.	0·025*N*-Soln. *k* termol. (min.$^{-1}$).
0	0·05	—	0·025	—
10	0·0372	16·2	0·0227	17·0
20	0·0317	14·9	0·0208	17·0
30	0·0285	13·9	0·0198	15·9
40	0·0265	12·8	0·0188	15·4
50	0·0250	12·0	0·0180	14·9
60	0·0238	11·4	0·0174	14·2

Fig. 2.



I. 0·05N-*a-Alanine* + 0·05*N*-HNO_2.
II. 0·025N- „ + 0·025*N*- „
III. 0·05N- „ + 0·05*N*- „ + 0·5*N*-KCl.

of passage of gas bubbles through the liquid. If any other simple order is assumed for the reaction, there is no kind of convergence of the *k* values; assuming a quadrimolecular reaction, which gives more constant values for *k* at any one dilution, the extrapolated

value for k at 0·05N is 390 min.$^{-1}$, and at 0·025N 720 min.$^{-1}$; and for a bimolecular reaction 0·78 at 0·05N and 0·43 at 0·025N.

Experiment showed that doubling the concentration of nitrous acid increased the rate of reaction much more than doubling the concentration of glycine. Hence of the three reacting molecular species, one must be glycine in some form and the other two nitrous acid; there is an immediate analogy with the case of methylamine, where the reaction velocity is proportional to the product $[RNH_3^{\cdot}][NO_2']$$[HNO_2]$.

α-Alanine and β-Alanine.—Precisely the same holds for these two acids, except that β-alanine reacts much less readily, so that in 0·025N-solution the velocity is too slow for accurate measurement. Measurements were therefore made in 0·05N- and 0·04N-solution. The results are shown in Figs. 2 and 3 and in Tables II and III.

TABLE II.

α-Alanine.

	0·05N-Soln.		0·025N-Soln.	
t min.	x norm.	k termol. (min.$^{-1}$).	x norm.	k termol. (min.$^{-1}$).
0	0·05	—	0·025	—
10	0·0401	11·1	0·0233	12·1
20	0·0354	10·0	0·0222	10·7
30	0·0326	9·0	0·0212	10·4
40	0·0306	8·4	0·0204	10·0
50	0·0290	7·6	0·0198	9·5
60	0·0279	7·4	0·0193	9·4

TABLE III.

β-Alanine.

	0·05N-Soln.		0·04N-Soln.	
t min.	x norm.	k termol. (min.$^{-1}$).	x norm.	k termol. (min.$^{-1}$).
0	0·05	—	0·04	—
10	0·0460	3·33	0·0380	3·40
20	0·0435	3·10	0·0364	3·25
30	0·0418	2·87	0·0350	3·16
40	0·0402	2·74	0·0339	3·07
50	0·0388	2·65	0·0329	2·99
60	0·0375	2·60	0·0321	2·88

Now an aliphatic amino-acid, $NH_2{\cdot}R{\cdot}CO{\cdot}OH$, in solution together with the weak acid nitrous acid exists almost entirely in the two forms $NH_3^+{\cdot}R{\cdot}CO{\cdot}O^-$ (A^{+-}) and $NH_3^+{\cdot}R{\cdot}CO{\cdot}OH$ (A^+) (Bjerrum, *Z. physikal. Chem.*, 1923, **104**, 147). If the total concentration of the amino-acid i[illegible] d and is x, and if a fraction f of the [illegible] ave

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. . . . . (1)

where K_s is the [illegible] e amino-acid and

$[H^{\cdot}]$ is the hydrogen-ion concentration. Further, since the whole solution is electrically neutral, $[NO_2'] = [H^{\cdot}] + [A^+]$, which gives

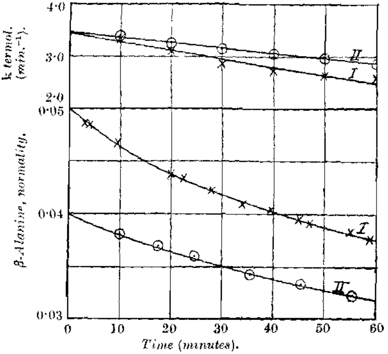
$$[NO_2'] = fx + [H^{\cdot}] \text{ and } [HNO_2] = (1 - f)x - [H^{\cdot}] \quad . \quad . \quad (2)$$

Therefore, if K_N is the dissociation constant of nitrous acid,

$$(fx + [H^{\cdot}])[H^{\cdot}]/\{(1 - f)x - [H^{\cdot}]\} = K_N \quad . \quad . \quad (3)$$

Elimination of $[H^{\cdot}]$ between equations (1) and (3) leads to a cubic equation connecting x and f. Numerical values were substituted for K_s, K_N and x, giving to the last the values $0{\cdot}05N$ and $0{\cdot}025N$

FIG. 3.



I. $0{\cdot}05N$-β-*Alanine* + $0{\cdot}05N \cdot HNO_2$.
II. $0{\cdot}04N$- ,, + $0{\cdot}04N$- ,,

successively, and values for $(1 - f)$ were calculated: these are shown in Table IV.

TABLE IV.

	K_s.	$(1-f)$, $0{\cdot}05N$.	$(1-f)$, $0{\cdot}025N$.	% Change.
Glycine	$4{\cdot}7 \times 10^{-3}$*	0·786	0·800	1·75
α-Alanine	$2{\cdot}45 \times 10^{-3}$*	0·721	0·718	0·43
β-Alanine	$2{\cdot}49 \times 10^{-4}$†	0·444	0·444	0

* Bjerrum, *loc. cit.*
† Calculated from Ley's results (*Ber.*, 1909, **42**, 374).

It can be seen that the fraction of the amino-acid present in either form hardly changes in value on alteration in concentration, and the assumption is made here that it is independent of concentration.

The form of the amino-acid which reacts with nitrous acid may be

A^+ or A^{+-} or both. Now addition of sulphuric acid lowers the reaction velocity; if A^+ is the reacting form, the concentration of this form will be increased by addition of mineral acid, and hence the nitrite ion must be involved in the reaction, since there is no other derivative of nitrous acid whose concentration is decreased by mineral acid.

If, however, A^{+-} is the reacting form, the concentration of this is decreased by increasing the hydrogen-ion concentration (compare equation 1), and thus the velocity may be proportional to the product $[A^{+-}][HNO_2]^2$. The measurement of reaction velocity in the presence of sulphuric acid shows that of all possible hypotheses the latter is correct.

The results of measurements with 0·05*N*-glycine and 0·05*N*-nitrous acid in the presence of 0·05*N*-sulphuric acid and of 0·1*N*-sulphuric acid are shown in curves III and IV of Fig. 1. Assuming that the reaction velocity is proportional to the product $[A^{+-}][HNO_2]^2$, let the concentration of glycine and of nitrous acid be a initially and x at time t. For the results shown in curve IV the amount of sulphuric acid present is $2a$; the hydrogen-ion concentration at time t may be taken as $2a-x$, since the glycine will be almost completely in the form A^+. Hence, if f is the fraction of glycine present as A^+, we have analogously with equation 1,

$$(1-f)x(2a-x)/fx = K_s,$$

whence $f = (2a-x)/(K_s + 2a - x)$. It can be further assumed that the nitrous acid is completely undissociated in the presence of the sulphuric acid, and thus on the above assumption we get for the reaction velocity

$$-dx/dt = kx^3K_s/(K_s + 2a - x),$$

which on integration between times t and 0 gives

$$k = \frac{1}{t}\left(\frac{a^2-x^2}{2a^2x^2} + \frac{a-x}{K_sx^2}\right).$$

Values of k calculated from this equation for every 10 minutes are shown in Table V.

For the reaction in the presence of one equivalent of sulphuric acid, after a certain time an appreciable amount of free sulphuric acid is present in the solution, since some glycine has disappeared. The hydrogen-ion concentration can be taken as equal to that of this free acid; thus at time t, $[H^{\cdot}] = (a-x)$. In a fashion similar to that above, it can be shown that

$$-dx/dt = kx^3K_s/(K_s + a - x).$$

This expression cannot be integrated back to the beginning, since

the assumptions made do not hold at the start of the reaction. Integration between times t_2 and t_1 gives

$$k = \frac{1}{t_2 - t_1}\left[\frac{K_8 + a}{2K_8x^2} - \frac{1}{K_8x}\right]_{x_1}^{x_2}.$$

Values of k calculated from this with $t_1 = 20$ mins. are shown in Table V.

Now for the reaction between glycine and nitrous acid alone, the fraction of glycine present in the form A^{+-} is given in Table IV; the concentration of undissociated nitrous acid is given by equation (2), since the term [H$^{\cdot}$] can be obtained from equation (1). Thus on the present assumption the reaction velocity should be given by

$$-\frac{dx}{dt} = k(1 - f)x\left(\overline{1 - f}x - \frac{K_8f}{1 - f}\right)^2$$

whence, assuming f is independent of concentration and writing $(1 - f) = b$ and $K_8f/(1 - f) = c$,

$$k = \frac{1}{bct}\left(\frac{1}{bx - c} - \frac{1}{ab - c} - \log_e \frac{x}{bx - c} \cdot \frac{ab - c}{a}\right) \quad . \quad . \quad (4)$$

Values of k calculated both for $0{\cdot}05N$- and $0{\cdot}025N$-solutions are shown in Table V.

It will be seen that the values of k from the four sets of experiments agree as well as could be expected. In the reactions which proceed more slowly, and thus where the spontaneous decomposition of the nitrous acid is less marked, the values of k are higher and fall off less rapidly.

TABLE V.

Glycine.

	$0{\cdot}05N$-Glycine + $0{\cdot}05N$-HNO_2.					$0{\cdot}025N$-Glycine + $0{\cdot}025N$-HNO_2.
	$0{\cdot}1N$-H_2SO_4.		$0{\cdot}05N$-H_2SO_4.		Alone.	
t.	x.	k.	x.	k.	k.	k.
0	0·0500	—	0·0500	—	—	—
10	0·0459	45·1	0·0411	—	39·2	45·0
20	0·0430	44·2	0·0357	—	33·5	40·3
30	0·0410	41·1	0·0332	32·8	29·4	37·5
40	0·0395	38·8	0·0311	28·5	27·9	34·2
50	0·0382	35·8	0·0300	25·7	26·5	33·1
	(Curve IV.)		(Curve III.)		(Curve I.)	(Curve II.)

If any other assumption is made as to the molecular species involved in the reaction, similar calculations can be carried out, and it is found that there is no kind of agreement between the values derived from the four sets of experiments.

Taking it as proved that the reaction velocity is proportional to the product $[A^{+-}][HNO_2]^2$, values for the true velocity coefficients for the three acids can be obtained from (4), plotted against time

and extrapolated to zero time. The results are in Table VI; they are not very accurate for the alanines because equation (4) is very sensitive to small changes in x, and the analytical method is not capable of the accuracy it demands.

TABLE VI.

	k (min.$^{-1}$).	K_S.
Glycine	46	$4{\cdot}7 \times 10^{-3}$
α-Alanine	32	$2{\cdot}45 \times 10^{-3}$
β-Alanine	45	$2{\cdot}49 \times 10^{-4}$

The apparent difference in the speeds of reaction in the three cases arises mainly from the difference in the acid dissociation constants K_S. A small value of K_S causes a small concentration of the form A^{+-} and therefore a small reaction velocity. The results of Dunn and Schmidt (*loc. cit.*) are thus in agreement with the general conclusions of Bjerrum (*loc. cit.*), that the more closely the amino- and the carboxyl group are situated in the carbon chain, the greater the value of K_S.

The possibility remains that the reaction may also proceed by an alternative mechanism, at a rate proportional to the product $[A^+][NO_2'][HNO_2]$ as in the case of methylamine and ammonia. If the velocity coefficient for this mechanism is of the same order as in those two cases, 1 min.$^{-1}$, the effect of this mechanism will be small compared with the "Zwitterion" mechanism, and the experimental accuracy is not great enough to detect it.

The results arrived at have two possible interpretations. Either the reaction is actually of the third order, or else it is a reaction between undissociated nitrous acid and a complex formed from the "Zwitterion" and nitrous acid, since the concentration of any such complex will be proportional to the product $[A^{+-}][HNO_2]$. Taking into account the results with methylamine, the latter explanation becomes the more probable; an uncharged complex can only arise in the case of methylamine from the molecular species $CH_3{\cdot}NH_3^+$ and NO_2'; in the amino-acids it can arise from the species A^{+-} and HNO_2; and in each case the reaction velocity is proportional to the product of the concentration of the appropriate molecular species multiplied by that of undissociated nitrous acid. The velocity coefficient is forty times larger in the amino-acids than in the amine; the difference, on this view, would be a measure of the ratio of the probabilities of the formation of a complex from the species A^{+-} and HNO_2 and from the ions RNH_3^+ and NO_2'.

Effect of Neutral Salts.

The effect of neutral salts is of interest because of the view of Pfeiffer that neutral salts and amino-acids form complexes which

exist in solution as well as in the solid state (references in Pfeiffer's "*Organische Molekulverbindungen*," 1927, p. 143 *et seq.*). His results indicate that calcium chloride is more able to form complexes than potassium chloride; but the reaction velocities in the presence of 0·05*N*-calcium chloride and of 0·05*N*-potassium chloride were found to be the same within the limits of error of the method. The retarding effect of neutral salts is also found in the cases of methylamine and ammonia, where it is almost certainly an ionic strength effect, and thus the present results provide no support for Pfeiffer's views.

Summary.

1. The velocity of reaction of nitrous acid with glycine, α-alanine, and β-alanine has been measured at 25° in dilute aqueous solution.

2. The reaction is approximately of the third order, and is retarded by the presence of neutral salts or of mineral acid.

3. It is shown that the principal reacting species are undissociated nitrous acid and the amino-acid in its "Zwitterion" form $NH_3^+\cdot R\cdot CO\cdot O^-$. The implications of this result are discussed.

My thanks are due to Mr. J. F. Cowley for his help during the preliminary experiments.

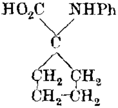
THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, May 31st,* 1928.]

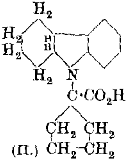
CCXLIX.—*The Condensation of Hexahydrocarbazole and of Tetrahydropentindole with* cyclo*Pentanone Cyanohydrin.*

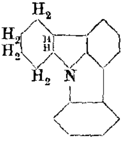
By SYDNEY GLENN PRESTON PLANT and DOROTHY MAY LYDDON RIPPON.

IT has been observed by Plant and Facer (J., 1925, **127**, 2037) that the fusion of 1-anilino*cyclo*pentane-1-carboxylic acid (I) with potassium hydroxide yields carbazole, a reaction which involves the enlargement of the *cyclo*pentane ring, since 1-*p*-toluidino- and 1-*o*-toluidino-*cyclo*pentane-1-carboxylic acid yield 3-methyl- and 1-methyl-carbazole, respectively, under similar conditions (Oakeshott and Plant, J., 1926, 1210; 1927, 484). A similar process, starting with certain heterocyclic bases in the place of aniline, might be expected to give polynuclear carbazole derivatives, *e.g.*, from 1-(9'-hexahydrocarbazyl)*cyclo*pentane-1-carboxylic acid (II) a substance of the structure (III) might arise. Manjunath (*J. Indian*

Chem. Soc., 1927, **4**, 271) has prepared substances * which clearly contain the ring system present in (III). By reducing 9-nitrosohexahydrocarbazole with zinc dust and acetic acid in the presence of *cyclo*hexanone he obtained 8 : 9-(1′ : 2′-*cyclo*hexyl)tetrahydro-

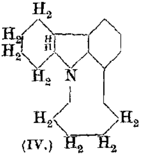

(I.)

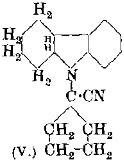

(II.)

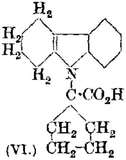

(III.)

carbazole, which, on electrolytic reduction, gave the corresponding 8 : 9-(1′ : 2′-*cyclo*hexyl)hexahydrocarbazole (IV).

Although, for reasons given below, it was not found possible during the course of the present work to synthesise a polynuclear carbazole of the type described, several interesting reactions have been brought to light. When hexahydrocarbazole (the ordinary *cis*-modification, m. p. 99°; see Gurney, Perkin, and Plant, J., 1927, 2676) was treated with *cyclo*pentanone and potassium cyanide in glacial acetic acid solution, 1-(9′-*hexahydrocarbazyl*)-1-*cyanocyclopentane* (V) resulted. This nitrile, on boiling with concentrated hydrochloric


(IV.)


(V.)


(VI.)

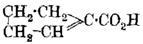
acid or with alcoholic hydrochloric acid, was hydrolysed with the formation of hexahydrocarbazole and *cyclo*pentanone, so this route to the corresponding acid could not be adopted. When a solution of the nitrile in concentrated sulphuric acid was left for two days, the corresponding *amide* was produced. Hydrolysis of this to the acid could not be carried out, the amide either remaining unchanged or breaking up with the production of hexahydrocarbazole under the conditions used. When the amide itself was heated with

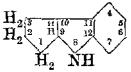
* The formulæ given for these substances in Manjunath's paper do not contain the ring system under discussion here and are obviously misprints, but there can be *no doubt* concerning the actual structure of the compounds described.

potassium hydroxide with a view to converting it directly into the polynuclear carbazole, it again broke up with the formation of hexahydrocarbazole.

As a possible alternative method for obtaining 1-(9′-hexahydrocarbazyl)*cyclo*pentane-1-carboxylic acid, the nitrosoamine of 1-anilino*cyclo*pentane-1-carboxylic acid (Plant and Facer, *loc. cit.*) was reduced with zinc dust and hot acetic acid in the presence of *cyclo*hexanone. This led to the formation of 1-(9′-*tetrahydrocarbazyl*)-*cyclopentane-1-carboxylic acid* (VI), but reduction to the corresponding derivative of hexahydrocarbazole has not been brought about. However, the acid has some interesting reactions. When warmed with 60% aqueous sulphuric acid, when distilled, or when heated with solid potassium hydroxide, it dissociates into tetrahydrocarbazole and Δ^1-*cyclo*pentene-1-carboxylic acid (VII). It has previously been observed that 1-anilino*cyclo*pentane-1-carboxylic acid, on heating, yields the lactone of 1-1′-hydroxy*cyclo*pentane-1′-carboxylylanilino*cyclo*pentane-1-carboxylic acid (Plant and Facer, *loc. cit.*); but 1-anilino*cyclo*hexane-1-carboxylic acid behaves differently on heating alone, giving aniline and Δ^1-*cyclo*hexene-1-carboxylic acid, and ψ-indoxyl*spirocyclo*hexane results on fusion with potassium hydroxide (Betts, Muspratt, and Plant, J., 1927, 1310). 1-(9′-Tetrahydrocarbazyl)*cyclo*pentane-1-carboxylic acid, on heating, behaves like 1-anilino*cyclo*hexane-1-carboxylic acid, but lactone formation is here impossible in the absence of an unsubstituted >NH group.

The unexpected course of some of the above reactions suggested an investigation of similar reactions with *tetrahydropentindole* (VIII).

(VII.) 

 (VIII.)

This base, which has been obtained by the electrolytic reduction of dihydropentindole, theoretically ought to exist in *cis*- and *trans*-modifications, analogous to the two forms of hexahydrocarbazole (see Gurney, Perkin, and Plant, *loc. cit.*); the *trans*-configuration, however, is very highly strained and its formation in appreciable quantities during the reduction of dihydropentindole is not to be expected. This point has been investigated, and the reduction product has been shown to consist essentially of a single substance, undoubtedly the *cis*-modification of tetrahydropentindole. It can be acetylated and benzoylated, and it is converted by the action of methyl iodide into 8-*methyltetrahydropentindole*, which yields a characteristic *methiodide*, m. p. 189°, that has been used for recognising tetrahydropentindole. When dissolved with *cyclo*pentanone

in glacial acetic acid and treated with potassium cyanide, tetrahydropentindole is converted into 1-(8′-*tetrahydropentindyl*)-1-*cyano*cyclo*pentane*. By a reaction analogous to that observed with the corresponding hexahydrocarbazole derivative, this nitrile is hydrolysed on boiling with concentrated hydrochloric acid with the formation of tetrahydropentindole and *cyclo*pentanone. In view of the ease with which these nitriles were hydrolysed it is interesting to point out that Kötz and Merkel (*J. pr. Chem.*, 1926, **113**, 75) observed that 1-piperidyl-1-cyano*cyclo*hexane was hydrolysed in a similar way, on boiling with aqueous-alcoholic potassium hydroxide. By allowing the solution of 1-(8′-tetrahydropentindyl)-1-cyano*cyclo*pentane in concentrated sulphuric acid to remain for two days, 1-(8′-*tetrahydropentindyl*)cyclo*pentane*-1-*carboxyamide* is produced. This amide decomposed with the formation of tetrahydropentindole when heated with solid potassium hydroxide. Many amides of this type seem to be hydrolysed to the corresponding acids only with difficulty, if at all (compare, *e.g.*, Kötz and Merkel, *loc. cit.*; Betts, Muspratt, and Plant, *loc. cit.*; Oakeshott and Plant, J., 1927, 492), and this fact, together with the alternative reactions outlined above, can account for the inability to prepare the acids from the amides described in the present work.

EXPERIMENTAL.

1-(9′-*Hexahydrocarbazyl*)-1-*cyano*cyclo*pentane* (V) soon began to separate when hexahydrocarbazole (21 g.), dissolved in a mixture of glacial acetic acid (210 c.c.) and *cyclo*pentanone (17·5 c.c.), was treated gradually with a solution of potassium cyanide (14 g.) in water (50 c.c.); after several hours, the mixture was diluted with water, and the product collected. It crystallised from dilute alcohol in colourless prisms, m. p. 76° (Found: N, 10·5. $C_{18}H_{22}N_2$ requires N, 10·5%).

A solution of this nitrile in an excess of concentrated hydrochloric acid was boiled under reflux for 3 hours and then distilled in steam for a short time. From the distillate, saturated with sodium chloride, ether extracted *cyclo*pentanone, b. p. 129—130°, which was identified by converting its phenylhydrazone into dihydropentindole (Perkin and Plant, J., 1923, **123**, 3242), m. p. and mixed m. p. 108°. The aqueous solution remaining after the steam distillation contained hexahydrocarbazole in good yield. The same reaction took place when the nitrile was boiled under reflux for 6 hours with alcohol saturated with hydrogen chloride.

1-(9′-*Hexahydrocarbazyl*)cyclo*pentane*-1-*carboxyamide*.—A solution of the nitrile (V) in concentrated sulphuric acid was kept for 2 days, poured on ice, and made alkaline with concentrated aqueous

ammonia. The solid product was ground with dilute aqueous ammonia to decompose any sulphate which might have been present, and then crystallised from alcohol, from which 1-(9′-*hexahydrocarbazyl*)cyclo*pentane*-1-*carboxyamide* was obtained in colourless plates, m. p. 160° (Found: N, 9·9. $C_{18}H_{24}ON_2$ requires N, 9·9%). This amide was not changed by boiling its solution in aqueous-alcoholic potassium hydroxide for 4 hours, or by heating it with 40% aqueous sulphuric acid. When its solution in concentrated hydrochloric acid was boiled under reflux for several hours, a considerable amount of hexahydrocarbazole was produced, which was removed from the solution, evaporated to small bulk and made alkaline with sodium hydroxide, by distillation in steam. When the amide was heated with powdered potassium hydroxide at 180—200°, in a copper tube fitted with a reflux air condenser, for 15 minutes, a considerable quantity of hexahydrocarbazole was produced. This was isolated by treating the cooled mixture with warm water and crystallising the precipitated solid from alcohol. The action of heat alone at 180—200° had no appreciable effect on the amide.

1-(9′-*Tetrahydrocarbazyl*)cyclo*pentane*-1-*carboxylic Acid* (VI).—The nitrosoamine of 1-anilino*cyclo*pentane-1-carboxylic acid (40 g., prepared as described by Plant and Facer, *loc. cit.*) was dissolved in a mixture of glacial acetic acid (560 c.c.) and water (240 c.c.), to which *cyclo*hexanone (56 c.c.) was added. With vigorous stirring, the mixture was warmed to 50°, and zinc dust (96 g.) was then gradually introduced, the temperature being raised slowly to 85°. The filtered solution was poured into *N*-sulphuric acid. When the solid product (yield, 25%) was crystallised from toluene, 1-(9′-*tetrahydrocarbazyl*)cyclo*pentane*-1-*carboxylic acid* separated in colourless prisms, m. p. 184° (Found: N, 5·0. $C_{18}H_{21}O_2N$ requires N, 4·9%).

When a solution of this acid (3 g.) in 60% aqueous sulphuric acid (180 c.c.) was left on the water-bath, crystals of Δ^1-*cyclo*pentene-1-carboxylic acid (m. p. and mixed m. p. 118°) gradually sublimed into the neck of the flask; dilution of the residual solution with water precipitated tetrahydrocarbazole. When a solution of 1-(9′-tetrahydrocarbazyl)*cyclo*pentane-1-carboxylic acid in cold concentrated sulphuric acid was left for several hours and then poured on ice, the acid was recovered unchanged. The acid resisted attempts to reduce it to the corresponding hexahydrocarbazole derivative by electrolytic reduction in alkaline solution, by sodium amalgam in alkaline solution, and by tin and alcoholic hydrochloric acid.

1-(9′-Tetrahydrocarbazyl)*cyclo*pentane-1-carboxylic acid was mixed with an excess of powdered potassium hydroxide and heated,

in a copper tube fitted with a reflux air condenser, at 320—340° for ½ hour. After cooling, the mixture was warmed with an excess of water. The insoluble portion, after crystallisation from aqueous alcohol, melted at 112° and was shown to be tetrahydrocarbazole by a mixed m. p. determination. The alkaline aqueous liquid, after filtering, was evaporated to a small volume, and acidified with concentrated hydrochloric acid, the mixture being kept cold. The solid which separated was crystallised from aqueous alcohol, Δ^1-*cyclo*pentene-1-carboxylic acid being obtained in colourless plates, m. p. 119° (Found: C, 64·1; H, 7·3. Calc.: C, 64·3; H, 7·1%). There is no doubt that this is identical with the Δ^1-*cyclo*pentene-1-carboxylic acid described by Haworth and Perkin (J., 1894, **65**, 101). A similar decomposition occurred on distilling 1-(9′ tetrahydrocarbazyl)*cyclo*pentane-1-carboxylic acid alone from a small distillation flask. The solid which collected in the side-tube yielded tetrahydrocarbazole (m. p. and mixed m. p. 114°) on treatment with dilute aqueous sodium hydroxide and filtration, and the alkaline filtrate, on evaporation to small bulk and acidification with concentrated hydrochloric acid, yielded Δ^1-*cyclo*pentene-1-carboxylic acid (m. p. and mixed m. p. 120°).

Tetrahydropentindole (VIII).—Dihydropentindole (5 g.) (Perkin and Plant, *loc. cit.*) was dissolved in sulphuric acid (140 c.c. of 60%) and submitted to electrolytic reduction at room temperature during 16 hours in the cathode compartment of an electrolytic cell, lead electrodes and a current of 5 amps. (0·03 amp. per sq. cm. of cathode) being used. From the solution, made alkaline with concentrated aqueous ammonia, ether extracted *tetrahydropentindole*, b. p. 152°/16 mm. (Found: C, 82·9; H, 8·3. $C_{11}H_{13}N$ requires C, 83·0; H, 8·2%). The tetrahydropentindole used in the present work was liquid, but a specimen was made to solidify and was found to melt at 21°.

A solution of tetrahydropentindole (3 g.) in hot acetic anhydride (30 c.c.) was boiled for 20 minutes, cooled, and shaken with water; the 8-*acetyltetrahydropentindole* obtained crystallised from alcohol in colourless prisms, m. p. 78° (Found: N, 6·9. $C_{13}H_{15}ON$ requires N, 7·0%). On shaking tetrahydropentindole (5 g.) with benzoyl chloride (5·5 g.) and an excess of dilute aqueous sodium hydroxide, 8-*benzoyltetrahydropentindole* separated as an oil, which gradually solidified; it crystallised from alcohol in colourless prisms, m. p. 86° (Found: N, 5·2. $C_{18}H_{17}ON$ requires N, 5·3%). When tetrahydropentindole (1·8 g.) and picric acid (2·5 g.) were mixed in hot toluene, the *picrate* separated; it crystallised from alcohol in yellow prisms, m. p. 159°.

8-*Methyltetrahydropentindole*.—An alcoholic solution of tetrahydropentindole (40 g.) and methyl iodide (45 g.) was boiled under reflux

for 24 hours, as much alcohol as possible was distilled off, and the residue was treated with an excess of dilute aqueous sodium carbonate and extracted with ether. After the extract had been dried over potassium carbonate and the solvent removed, the residual oil was boiled with an excess of acetic anhydride under reflux for an hour in order to acetylate any unchanged tetrahydropentindole. The cooled solution was shaken with an excess of water, concentrated hydrochloric acid (50 c.c.) added after 12 hours, the 8-acetyltetrahydropentindole removed by shaking twice with ether, and the aqueous solution made alkaline with sodium hydroxide and extracted with ether, which removed *8-methyltetrahydropentindole*, b. p. 136—137°/15 mm. (Found: N, 7·8. $C_{12}H_{15}N$ requires N, 8·1%). From a solution of this (2 g.) and picric acid (2·6 g.) in hot alcohol, the *picrate* separated in yellowish-green plates, m. p. 116°, on cooling. When 8-methyltetrahydropentindole or tetrahydropentindole was warmed in alcohol with an excess of methyl iodide the *methiodide* of 8-methyltetrahydropentindole slowly separated in colourless prisms, m. p. 189° (Found: I, 40·2. $C_{13}H_{18}NI$ requires I, 40·3%).

*1-(8'-Tetrahydropentindyl)-1-cyano*cyclo*pentane*.—A solution of tetrahydropentindole (37 g.) and *cyclo*pentanone (25 c.c.) in glacial acetic acid was treated with a concentrated aqueous solution of potassium cyanide (27 g.). After several hours, the solution was poured into an excess of water and the oily product, which solidified when rubbed, was recrystallised from alcohol, *1-(8'-tetrahydropentindyl)-1-cyano*cyclo*pentane* being obtained in colourless prisms, m. p. 51° (Found: N, 11·4. $C_{17}H_{20}N_2$ requires N, 11·1%). When this nitrile (1 g.) was mixed with picric acid (1·1 g.) in hot alcohol, and the solution was left, the *picrate* separated gradually in yellow prisms, m. p. 126°.

A solution of 1-(8'-tetrahydropentindyl)-1-cyano*cyclo*pentane in concentrated hydrochloric acid was boiled under reflux for 3 hours, and then submitted to steam distillation. From the distillate, ether extracted *cyclo*pentanone (identified by conversion into dihydropentindole as before). The acid solution, after being made alkaline with sodium hydroxide, was again submitted to steam distillation; the tetrahydropentindole isolated from the distillate by means of ether was identified by conversion into 8-methyltetrahydropentindole methiodide.

*1-(8'-Tetrahydropentindyl)*cyclo*pentane-1-carboxyamide*.—A solution of 1-(8'-tetrahydropentindyl)-1-cyano*cyclo*pentane in concentrated sulphuric acid was after 2 days poured on ice, and made alkaline with concentrated aqueous ammonia while being kept cool. The product, after being ground with dilute aqueous ammonia, was crystallised from alcohol, *1-(8'-tetrahydropentindyl)*cyclo*pentane-1-*

carboxyamide separating in colourless prisms, m. p. 130° (Found : N, 10·3. $C_{17}H_{22}ON_2$ requires N, 10·4%).

A mixture of this amide with powdered potassium hydroxide was heated at 280—315° for ½ hour, and, after cooling, was treated with water and submitted to steam distillation. From the distillate, ether extracted tetrahydropentindole (identified by converting it into 8-methyltetrahydropentindole methiodide). No tetrahydropentindole could be detected when this amide was heated alone at 280—315° for ½ hour. Attempts to hydrolyse the amide to the corresponding acid by boiling its solution in concentrated hydrochloric acid or in aqueous sulphuric acid were not successful.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, April 28th*, 1928.]

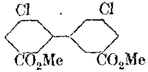
CCL.—*The Molecular Configurations of Polynuclear Aromatic Compounds. Part VII.* 5 : 5′-*Dichlorodiphenyl*-3 : 3′-*dicarboxylic Acid.*

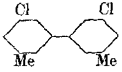
By FRED BRIDGES MCALISTER and JAMES KENNER.

FOR reasons which have been fully set out elsewhere (Kenner, *Chem. and Ind.*, 1927, **46**, 218), it was of importance to synthesise and examine a diphenyldicarboxylic acid isomeric with one of the 6 : 6′-diphenic acids, of which the asymmetry has been demonstrated (J., 1922, **121**, 614; 1923, **123**, 779, 1948; 1926, 470, 671), and carrying its substituents in the 3-, 3′-, 5-, and 5′-positions. 5 : 5′-Dinitrodiphenyl-3 : 3′-dicarboxylic acid having been found to be inaccessible by the usual method of synthesis, attention was directed to the corresponding dihalogenated acids. In this direction the facility with which 3-bromo-5-nitro-*p*-toluidine is available (Neville and Winther, *Ber.*, 1880, **13**, 968) suggested 5 : 5′-dibromodiphenyl-3 : 3′-dicarboxylic acid as the most suitable objective. However, bromine as well as iodine was eliminated when either -*bromo*-5-*iodotoluene* or *methyl* 3-*bromo*-5-*iodobenzoate* was heated with copper powder, so that no definite diphenyl derivative could be synthesised from either of them.

Finally, therefore, the more laborious preparation of 3-*chloro*-5-*iodotoluene* and of *methyl* 3-*chloro*-5-*iodobenzoate* was undertaken, and from each of these compounds the desired diphenyl derivative was obtained. Even in the latter case, however, the *methyl* 5 : 5′-*dichlorodiphenyl*-3 : 3′-*dicarboxylate* (I) underwent decomposition, so that the compound could only be obtained in poor yields under carefully regulated conditions, and, although, on the other hand, 5 : 5′-*dichloro*-3 : 3′-*ditolyl* (II) was readily isolated, it proved to be

of no value for the present purpose since it could not be readily oxidised to the corresponding dicarboxylic acid.

(I.) 

 (II.)

The *brucine*, *quinine*, and *acid morphine* salts of 5 : 5′-*dichlorodiphenyl*-3 : 3′-*dicarboxylic acid* were each found to be uniform, and the solutions of ammonium 5 : 5′-dichlorodiphenyl-3 : 3′-dicarboxylate prepared from them were in each case optically inactive. It would therefore appear that the acid has not the asymmetry of its 2 : 2′-6 : 6′-structural isomeride.

EXPERIMENTAL.

5-*Iodo*-3-*nitrobenzoic Acid*. (Experiments carried out by F. Allsop in the University of Sheffield.)—The usual procedure for the replacement of the amino-group by iodine yielded unsatisfactory results in this instance, but excellent yields were obtained in the following way. An intimate mixture of 5-nitro-3-aminobenzoic acid (5 g.) with potassium metabisulphite (3 g.) was slowly added to fuming nitric acid (12 c.c.) below $-2°$. After 2 hours, the solution was diluted with ice (60 g.) and then gradually treated with a solution of potassium iodide (8 g.) and iodine (4 g.) in water (8 c.c.). After 12 hours, the mixture was heated on the steam-bath, and the excess of iodine destroyed by addition of sodium bisulphite. By crystallisation from light petroleum, the *acid* was obtained in long prisms, m. p. 166—167° (Found: N, 4·8. $C_7H_4O_4NI$ requires N, 4·8%). The *ethyl* ester consisted of long prisms, m. p. 59—60° (Found: N, 4·4. $C_9H_8O_4NI$ requires N, 4·4%). Repeated attempts to prepare a diphenyl derivative from the ester in the usual manner were unsuccessful.

3-*Bromo*-5-*iodotoluene*.—When a solution of potassium iodide (24 g.) in water (40 c.c.) was gradually added to a diazonium salt solution prepared from 5-bromo-*m*-toluidine (18 g.), sulphuric acid (12 c.c.), water (120 c.c.), and sodium nitrite (8 g.), the violence of decomposition of the resultant diazonium iodide was such as to project the material from the containing vessel. In subsequent preparations, this difficulty was overcome by carrying out the mixing of the respective solutions, and the subsequent decomposition, in small aliquot proportions. 3-*Bromo*-5-*iodotoluene* boiled at 150°/29 mm. and melted at 23° (Found: X,* 141·6. C_7H_6BrI requires X, 142·4).

* X denotes weight of mixed silver halides expressed as a percentage of the weight of material analysed.

3-Bromo-5-acetamidobenzoic acid, prepared by the oxidation of *5-bromoaceto*-m-*toluidide*, m. p. 171—172° (33·5 g.), with a solution of potassium permanganate (72 g.) and hydrated magnesium sulphate (48 g.) in water (6000 c.c.), melted at 279—281° (Found: N, 5·5. $C_9H_8O_3NBr$ requires N, 5·4%).

5-Bromo-3-aminobenzoic acid was obtained in the form of its hydrochloride by boiling a solution of the acetyl derivative (5 g.) in concentrated hydrochloric acid (50 c.c.) for one hour and then evaporating it. The acid, liberated by means of sodium acetate, separated from dilute alcohol in colourless needles, m. p. 220—222° after softening at 194° (Found: N, 6·5. $C_7H_6O_2NBr$ requires N, 6·5%).

3-Bromo-5-iodobenzoic acid was prepared from the hydrochloride of 5-bromo-3-aminobenzoic acid in the usual manner and melted at 209—211° (Found: X, 128·6. $C_7H_4O_2BrI$ requires X, 129·3). The *methyl* ester separated from benzene in small orange prisms, m. p. 59—61° (Found: X, 123·1. $C_8H_6O_2BrI$ requires X, 124·0).

3-Chloro-5-iodotoluene, prepared with the precautions explained in the case of the corresponding bromo-derivative, boiled at 138—140°/26 mm. and melted at 0° (Found: X, 149·4. C_7H_6ClI requires X, 149·5).

5 : 5'-Dichloro-3 : 3'-ditolyl was readily prepared by gradually adding copper powder during ½ hour to an equal weight of 3-chloro-5-iodotoluene at 250—260°, finally raising the temperature to 290°, and then allowing the product to cool. After crystallisation from alcohol, it melted at 101—102° (Found: Cl, 27·8. $C_{14}H_{12}Cl_2$ requires Cl, 28·4%). Experiments on its oxidation with dilute nitric acid (Cohen and Dakin, J., 1901, **79**, 1124) or neutral or alkaline permanganate led to no satisfactory result.

3-Chloro-5-acetamidobenzoic acid, m. p. 265—267° (Found: N, 6·55; *M*, 213·9. $C_9H_8O_3NCl$ requires N, 6·6%; *M*, 214·5), and *3-chloro-5-aminobenzoic acid hydrochloride*, m. p. 118—121° (Found: N, 6·65. $C_7H_7O_2NCl_2$ requires N, 6·7%), were prepared in the manner adopted for the bromo-derivatives. In place, however, of the ordinary procedure, the following was a much more satisfactory method of preparing *3-chloro-5-iodobenzoic acid*: A finely ground mixture of 3-chloro-5-aminobenzoic acid hydrochloride (30 g.) with potassium metabisulphite (16·2 g.) was gradually added below 0° to nitric acid (78 c.c.; *d* 1·5). After 4 hours, the mixture was poured on ice (240 g.) and gradually treated with a solution of iodine (22·2 g.) and potassium iodide (43·2 g.) in water (40 c.c.). The acid crystallised from dilute alcohol in reddish-yellow needles, m. p. 190—191° (Found: X, 133·5; *M*, 281. $C_7H_4O_2ClI$ requires X, 134·2; *M*, 282·4). Its *methyl* ester crystallised from methyl

cohol in orange needles, m. p. 43—44° (Found: X, 127·0. $_8H_6O_2ClI$ requires X, 127·9).

Methyl 5 : 5′-*dichlorodiphenyl*-3 : 3′-*dicarboxylate* was obtained when opper powder was gradually added to an equal weight of methyl ·chloro-5-iodobenzoate at 265—270°, and the mixture was then eated for 10 minutes at 270°. For the success of the preparation he copper powder must be added as quickly as possible consistent ith the maintenance of the temperature within the limits indicated, ince prolonged or over-heating causes decomposition. Even in the nost favourable circumstances the yield could not be raised above 5%. The ester separated from benzene in small cubical crystals, n. p. 156° (Found: Cl, 21·5. $C_{16}H_{12}O_4Cl_2$ requires Cl, 21·2%).

5 : 5′-*Dichlorodiphenyl*-3 : 3′-*dicarboxylic acid*, prepared from its ster by means of aqueous sodium hydroxide, was practically nsoluble in the ordinary solvents and was sparingly soluble in glacial acetic acid. From this it crystallised in nodules, m. p. 358—360° (Found: Cl, 23·2. $C_{14}H_8O_4Cl_2$ requires Cl, 23·1%).

The *brucine* salt crystallised from methyl alcohol in radiate clusters of small prisms, m. p. 178—179°, decomp. 191—193° (Found: N, 5·1. $C_{60}H_{60}O_{12}N_4Cl_2$ requires N, 5·1%). For a 0·78% solution in chloroform, $[\alpha]_D = -5{\cdot}2°$.

The *quinine* salt separated from methyl alcohol in small prisms, m. p. 170—172°, decomp. 174° (Found: N, 5·8. $C_{54}H_{60}O_4N_4Cl_2$ requires N, 5·85%). They were insoluble in acetone, chloroform, and ether, and only sparingly soluble in methyl or ethyl alcohol. For a 0·18% solution in absolute alcohol, $[\alpha]_D = -132°$.

The *acid morphine* salt crystallised from methyl alcohol in small nodules, m. p. 218—219°, decomp. 223—225° (Found: N, 2·4. $C_{31}H_{27}O_7NCl_2$ requires N, 2·4%). The salt was almost insoluble in benzene, chloroform, acetone, and ether, and sparingly soluble in methyl or ethyl alcohol. For a 0·20% solution in ethyl alcohol, $[\alpha]_D = -30°$.

Solutions of the ammonium salt were prepared from both the brucine and the quinine salt by shaking them with chloroform and dilute ammonia solution, but in the case of the acid morphine salt dilute ammonia alone was employed, the bulk of the morphine being then removed by filtration, and the last traces by means of chloroform. In each case the solutions obtained were optically inactive. The quinidine salt was an oil, easily soluble in methyl alcohol and acetone, sparingly in ether or benzene. The cinchonine salt was a gum, readily soluble in chloroform, water, and methyl alcohol, but very sparingly soluble in benzene or ether, and could not be obtained in the solid condition.

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CCLI.—*The Apparent Hydration of Ions. Part I. The Densities and Viscosities of Saturated Solutions of Sodium and Potassium Chlorides in Hydrochloric Acid.*

By JOHN WILLIAM INGHAM.

A REVIEW of the determined values of the hydration numbers of strong electrolytes in aqueous solutions shows that, whilst there is a certain unanimity with respect to the alkali chlorides and their ions, there is considerable doubt as to the relative position of the hydrogen ion.

Recent work by Sugden (J., 1926, 174), who studied the distribution of acetic acid between aqueous solutions of salts and amyl alcohol, and of Glasstone and his collaborators (J., 1925, **127**, 2660; 1926, 2935, 2939; 1927, 635), using the salting-out effect upon ethyl acetate and aniline, confirms much earlier work, to which these authors refer, in establishing the series $Li^{\cdot} > Na^{\cdot} > K^{\cdot}$, although the two methods give numerically different results for the hydration numbers:

	LiCl.	NaCl.	KCl.
Sugden	10·5	7·9	3·4
Glasstone	27	24	22

Sugden finds the chlorine ion to be non-hydrated, so his values for the salts are also those of the kations; on the other hand, Glasstone finds 10 for Cl′, the corresponding kation values being $Li^{\cdot}$ 17, $Na^{\cdot}$ 14, $K^{\cdot}$ 12. These "hydration numbers" of Glasstone are for ions at infinite dilution, smaller values being found for higher concentrations. Sugden obtained reasonably constant values over a range of concentration *N*—*N*/10.

Neither of these methods is suitable for comparative determination with hydrochloric acid, the relative position of which has been found by other methods (for references, see General Discussion upon the Theory of Strong Electrolytes, *Trans. Faraday Soc.*, 1927, **23**). Remy (*ibid.*, p. 381) deduces from mobilities the values $H^{\cdot}$ 0·9, $K^{\cdot}$ 4·1, $Na^{\cdot}$ 7·4, $Li^{\cdot}$ 12·6 for the "water-sheaths" of these ions, Cl′ having the value 3 dependent upon the assumption that large organic ions have no sheaths. Scatchard (*ibid.*, p. 454; *J. Amer. Chem. Soc.*, 1925, **47**, 2098; 1927, **49**, 217), from calculations of activities in water–alcohol solutions, concludes that lithium, sodium, potassium, and chlorine ions are not "chemically hydrated," but that the hydrogen ion may be present in the form $H_3O^{\cdot}$. This conception of the hydrogen ion has been used also by Fajans (*Trans. Faraday Soc.*, 1927, **23**, 357) in dealing with refractometric measure-

ments upon hydrochloric acid solutions. It is necessary to distinguish between "chemical hydration" and the more general attraction between ions and solvent ("solvation"), such as is assumed to lead to the presence of aggregates of water molecules with ions as centres (compare Scatchard, *loc. cit.*).

Bjerrum (*Z. anorg. Chem.*, 1920, **109**, 275) calculated from heats of dilution that hydrochloric acid is associated with 8 molecules of water and that sodium and potassium chlorides are relatively non-solvated. It appears that some methods detect only chemical hydration and that others which indicate solvation as well have not yet been satisfactorily correlated.

The extension to concentrated solutions by Hückel (*Physikal. Z.*, 1925, **26**, 93) of the original theory of complete dissociation of strong electrolytes (Debye and Hückel, *ibid.*, 1923, **24**, 185), and the work of Harned (*J. Amer. Chem. Soc.*, 1926, **48**, 326) upon the activity of hydrochloric acid in concentrated solutions of lithium, sodium, and potassium chlorides, supporting the extended theory, have prepared the way for the examination of other properties of such solutions. The work now described is a contribution in this direction.

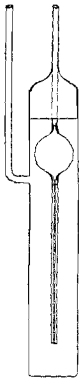
The solubilities of potassium and sodium chlorides in hydrochloric acid solutions of concentrations varying between the widest limits have been determined, together with the densities and viscosities of the solutions, all at 25°. Previous measurements of the solubilities of alkali chlorides in hydrochloric acid have been made at 0° by Engel (*Compt. rend.*, 1886, **102**, 113, 619) and at 30° by Masson (J., 1911, **99**, 1132). Others, including Armstrong and Eyre (*Proc. Roy. Soc.*, 1907, *A*, **79**, 564 *et seq.*) and Gibson and Denison (*Proc. Roy. Soc. Edin.*, 1911, **30**, 562), have studied in a more general way the precipitating action of the acid. A full review is given in the Reports of the British Association of 1910 and 1911 in the sections on Solubility. The viscosities do not appear to have been measured for such mixtures.

Determination of Viscosities.

The method adopted was that due to Scarpa (*Gazzetta*, 1910, **40**, 271) with a viscometer (Fig. 1) similar to that used by Farrow (J., 1912, **101**, 347). The dimensions of the apparatus were: bulb 5 c.c., capillary length 10 cm., bore 0·4 mm.; the lower end of the capillary stood 2 cm. above the bottom of the outer cylindrical vessel, which was 3 cm. in diameter. The rest of the apparatus (negative pressure device and manometer) was like that of Farrow except that a three-way stopcock was added in order to facilitate the operations.

The viscometer was standardised with conductivity water at $25° \pm 0{\cdot}02°$, with a negative pressure of 300 mm. on the gauge, absolute alcohol being used as the gauge indicator liquid. The constant of the apparatus was thus determined, using the expression $k = \eta_w/[t_1t_2/(t_1 + t_2)]_w$, η_w, the coefficient of viscosity of water, being taken as 0·0891 (Thorpe and Rodger), and t_1 and t_2 being the times of flow upwards under the applied negative pressure and downwards by gravity. Rigorous precautions of cleanliness were taken throughout the whole of the experiments, and corrections were applied for variations in temperature of the gauge liquid which stood outside the thermostat. The constant of the viscometer was independent of the amount of water used in the outer vessel to within 0·1%, and was reproducible with this accuracy at intervals during the subsequent measurements with the solutions. It was also shown that a layer of well-washed garnets placed below the end of the capillary tube, even to a depth of 1 cm., had no influence on the constant: so that, in the case of solutions, any small layer of undissolved solid would have no effect in this way.

FIG. 1.



The apparatus was tested by determinations upon a sample of absolute alcohol ($d^{25°}_{4°}$ 0·78711) and comparisons were made with values found for the same liquid in (i) an ordinary Ostwald viscometer and (ii) an Ostwald constant-pressure viscometer, in the same thermostat. The results were:

η (Scarpa) 0·01107; η (Ostwald, i) 0·01108; η (Ostwald, ii) 0·01106.

With a higher negative pressure of 400 mm. the Scarpa method gave a lower value, *viz.*, 0·01098. It appeared that the Scarpa method, with a gauge pressure of 300 mm., would be accurate to 0·1% compared with the Ostwald ordinary method. (The adjustments required in the Ostwald constant-pressure method are tedious, and it seems likely that the Scarpa method could conveniently replace it when a method not requiring density measurements is required.)

Recently, King and Partington (*Trans. Faraday Soc.*, 1927, **23**, 528), using the Scarpa method with a different design of tube, found difficulty in obtaining satisfactory agreement with the Ostwald method carried out in the same tube. For some of their salt solutions values as much as 6% higher were calculated from the former, and for a sample of alcohol ($d^{25°}_{4°}$ 0·78507) they gave

η (Scarpa) 0·01065; η (Ostwald) 0·01071.

Whilst no explanation of these discrepancies can be offered, they should not be taken as reflecting on the accuracy of the present work, the results of which afford a testimony to the usefulness of the method.

For the determinations upon the salt and acid mixtures, the acid solution of approximately known strength, prepared from a stock of specially distilled acid, was heated in a flask on a water-bath at 50—60° with a moderate excess of the pure salt, and the saturated solution was subsequently brought to equilibrium by shaking in the thermostat at 25° ± 0·02°. A quantity of 35—40 c.c. of solution, together with a little of the salt, was then quickly poured into the viscometer vessel, which was stoppered and had a glass stirrer. The final equilibrium was thus attained in the viscometer, and before the introduction of the capillary tube, slightly warmed, any suspended salt crystals were allowed to settle. Even with the strongest and densest solutions a perfectly clear solution was readily obtainable. The times of flow, measured to 0·2 sec., were usually constant after the first run, and only infrequently was any trouble experienced due to crystals finding their way into the capillary. The viscosity was calculated from $\eta_s = k \times [t_1 t_2/(t_1 + t_2)]_s$, the appropriate value of k for the observed gauge temperature being used.

Density determinations were made by pipetting with a warmed pipette sufficient liquid to fill a 25 c.c. density bottle which was suspended in the thermostat. The bottle had a cap over the stopper and was calibrated with pure water. The contents of the bottle were suitably diluted, and the acid was estimated by titration and the total chloride by weighing as silver chloride.

Redeterminations of the viscosities were frequently made upon the liquid remaining after the first withdrawal, with or without fresh additions, and the value was found to be unaltered and independent of the amount of liquid in the outer vessel. The usual order of agreement was to 0·1%, and the variation never exceeded 0·3%.

All apparatus used in the analyses was carefully calibrated and duplicate determinations were made, the total chloride estimations agreeing at least to 0·05%. The salts were tested and proved to be very pure. Acid solutions of high concentration were obtained by generating pure dry hydrogen chloride from the stock acid by a method which was shown to give no contamination with sulphuric acid.

In Table I are the results for solutions containing potassium chloride. In col. 1 are the absolute densities, $d_{4^\circ}^{25^\circ} = 0{\cdot}99707\frac{w'}{w} - \left[\frac{0{\cdot}0012(w' - w)}{w}\right]$; in col. 2 is η, the coefficient of viscosity (in c.g.s.

units); cols. 3, 4, and 5 respectively give molar concentrations of acid, salt and total solute; col. 6 the molar concentration of water (H_2O = 18·016); col. 7 is the sum of cols. 5 and 6.

Table II gives the data for solutions saturated with sodium chloride; and at the end are given the comparative values for pure water and for one solution of pure acid with no salt.

TABLE I.

$d_{4^\circ}^{25^\circ}$.	η.	*HCl.*	KCl.	Total solute.	H_2O.	Total solution.
1·1781	0·009710	—	4·199	4·199	48·00	52·20
1·1671	0·009918	0·464	3·748	4·212	48·32	52·53
1·1564	0·01020	0·990	3·288	4·278	48·56	52·84
1·1467	0·01044	1·492	2·887	4·379	48·67	53·05
1·1419	0·01063	1·833	2·604	4·436	48·90	53·34
1·1272	0·01109	2·743	1·951	4·694	48·95	53·64
1·1191	0·01155	3·570	1·449	5·020	48·90	53·92
1·1169	0·01178	4·008	1·227	5·235	48·81	54·04
1·1150	0·01216	4·665	0·963	5·608	48·50	54·11
1·1169	0·01279	5·672	0·607	6·279	48·01	54·29
1·1272	0·01380	7·144	0·309	7·453	46·27	53·72
1·1423	0·01519	8·433	0·267	8·700	45·22	53·92
1·1713	0·01788	10·68	0·215	10·89	42·52	53·41
1·1855	0·01943	11·74	0·20	11·94	41·22	53·16
1·1863	0·01952	11·81	0·22	12·03	41·04	53·06
1·2009	0·02121	12·96	0·24	13·19	39·46	52·65

TABLE II.

			NaCl.			
1·1981	0·01779	—	*5·4325*	*5·4325*	48·85	54·28
1·1867	0·01694	0·503	4·880	5·383	49·03	54·41
1·1781	0·01641	0·886	4·483	5·369	49·06	54·43
1·1511	0·01492	2·265	3·149	5·414	49·10	54·52
1·1352	0·01419	3·185	2·310	5·495	49·08	54·58
1·1319	0·01405	3·487	2·079	5·566	48·98	54·55
1·1282	0·01391	3·830	1·797	5·627	49·05	54·68
1·1200	0·01358	4·500	1·333	5·834	48·73	54·56
1·1160	0·01353	5·253	0·907	6·159	48·38	54·54
1·1158	0·01357	6·101	0·544	6·645	47·83	54·47
1·1213	0·01400	7·073	0·293	7·366	46·98	54·35
1·1302	0·01463	7·976	0·158	8·134	46·08	54·21
1·1458	0·01582	9·236	0·091	9·327	44·62	53·95
1·1970	0·02111	13·41	0·017	13·43	39·24	52·67
0·99707	0·00891	—	—	—	55·35	55·35
1·1203	0·01402	7·673	—	7·673	46·66	54·33

Discussion of Results.

Density and Volume Relations.—The changes which take place when acid replaces salt in the solutions can be expressed in terms of the molecular and ionic solution volumes of the constituents. In view of the order of ionic sizes as deduced from crystal lattice measurements by Wasastjerna (*Soc. Sci. Fenn. Comm. Phys. Math.*, 1923, **38**, 1), the various species to be considered would fall in series $H^{\cdot} < Na^{\cdot} < K^{\cdot} < H_2O < HCl < NaCl < KCl$, and the hydrogen

ion may be assumed to have negligible volume, or, if combined in the form $H_3O^{\cdot}$, it may provisionally be put equal to O'' or to H_2O.

The first addition of acid to the saturated sodium chloride solution results in a slight decrease in the total chloride (Table II, col. 5), accompanied by a small increase in water concentration and in the total number of molecules per litre (cols. 6 and 7). Rather more than an equivalent of salt is precipitated and hence there is more room for water to enter.

With further additions of acid the total solute concentration rises and, as the main factor influencing the volume effects is the chlorine ion (or radical), the amount of water which can remain begins to fall. The increase in chlorine-ion concentration more than balances the effect due to the decrease in sodium-ion concentration.

The volume effects are accompanied by mass changes reflected in the densities and this value falls at first, reaches a minimum, and then rises when the mass influence of the increasing chlorine-ion concentration preponderates.

The case for the potassium chloride mixtures is slightly different, and there is no lowering of the total solute content on the first addition of acid to the saturated solution of the pure salt. The removal of the larger potassium ions (compared with sodium ions), more nearly equal in size to water molecules, allows more room for chlorine accompanying hydrogen. The total solute concentration and the total number of molecules per litre both increase, and this continues until most of the potassium has been removed. Then, first the water concentration, and subsequently the total number of molecules, diminish as with the sodium chloride solutions. The mass effects again show in the densities, but the minimum occurs at a lower salt concentration. It can be seen that potassium chloride is not completely precipitated, and at the end of the series in solutions of high acid concentration it is still appreciably soluble, there being actually a slight increase in solubility.

The solubility effects thus appear to be dependent to a large degree upon the volumes in these series of mixed solutions of high concentration.

The above considerations can be extended in a quantitative way. Masson (*loc. cit.*) used an expression of the form $d = K + k_1a + k_2b$ to connect the densities with the molar concentrations of acid (a) and salt (b), K, k_1, and k_2 being constants. The constants k_1 and k_2 represent terms such as $(M - \alpha d_w)/1000$, where M is the molecular weight of the acid or salt, α the molar solution volume, and

d_w the density of the solvent in solution. The equation may be rewritten:

$$1000(d_{4^\circ}^{25^\circ} - d_w) = a(M_a - \alpha d_w) + b(M_b - \beta d_w).$$

This gives the difference in mass of one litre of solution and the same volume of water of the same apparent density as that in the solution. Thence also:

$$d_{4^\circ}^{25^\circ} = d_w + (a/1000)(M_a - \alpha d_w) + (b/1000)(M_b - \beta d_w).$$

Masson's conclusion, that the molecular solution volumes of water, salt, and acid remain constant over considerable ranges, is borne out.

Instead of the above formula, there may be substituted for it a similar expression in which the ionic solution volumes are used instead of the molecular values of the acid and salt. This reads

$$d_{4^\circ}^{25^\circ} = K + 0{\cdot}001a + k_2'b + k_3c.$$

K is the same as before, and since the ionic volume of the hydrogen ion is very small and its mass is approximately unity, k_1' has become 0·001, a, b, and c being the concentrations of hydrogen (ion), sodium (ion), and chlorine (ion) respectively. The data have been tested and constants deduced for this formula. The constants were first determined for the sodium chloride series, and it was then found that only k_2' had to be changed in order to obtain agreement with the data for potassium chloride. Having determined k_2' for each salt, the constants for the simpler formula of Masson could be obtained by direct summation, since for this equation

$$k_1 = 0{\cdot}001 + k_3 \text{ for the acid } (H^{\cdot} + Cl'),$$
$$k_2 = k_2' + k_3 \text{ for the salt } (Na^{\cdot} + Cl').$$

The two formulæ give, of course, practically identical results when tested on the same data, and hold good for each series as far as the point of minimum density. Tables III and IV give the results of these calculations, the appropriate values of the constants being included.

TABLE III. (NaCl.)

(i) $d_{4^\circ}^{25^\circ} = 1{\cdot}01275 + 0{\cdot}001a + 0{\cdot}0214b + 0{\cdot}01275c.$
(ii) $d_{4^\circ}^{25^\circ} = 1{\cdot}01275 + 0{\cdot}01375a + 0{\cdot}03415b.$

a.	$d_{4^\circ}^{25^\circ}$ (obs.).	$d_{4^\circ}^{25^\circ}$ (calc.).	a.	$d_{4^\circ}^{25^\circ}$ (obs.).	$d_{4^\circ}^{25^\circ}$ (calc.).
0	1·1981	1·1982	3·830	1·1282	1·1268
0·503	1·1867	1·1866	4·500	1·1200	1·1201
0·886	1·1781	1·1780	5·253	1·1160	1·1160
2·265	1·1511	1·1514	6·101	1·1158	1·1152
3·185	1·1352	1·1354	7·073	1·1213	1·1200
3·487	1·1319	1·1317	7·976		

TABLE IV. (KCl.)

(i) $d_{4°}^{25°} = 1{\cdot}01275 + 0{\cdot}001a + 0{\cdot}0267b + 0{\cdot}01275c$.

(ii) $d_{4°}^{25°} = 1{\cdot}01275 + 0{\cdot}01375a + 0{\cdot}03945b$.

a	$d_{4°}^{25°}$ (obs.).	$d_{4°}^{25°}$ (calc.).	a.	$d_{4°}^{25°}$ (obs.).	$d_{4°}^{25°}$ (calc).
0	1·1779	1·1783	3·570	1·1191	1·1190
0·464	1·1671	1·1670	4·008	1·1169	1·1163
0·990	1·1564	1·1561	4·665	1·1150	1·1149
1·492	1·1467	1·1471	5·672	1·1169	1·1147
1·832	1·1419	1·1408	7·144	1·1272	1·1232
2·743	1·1272	1·1274			

It appears that if the ionic solution volumes of the constituents remain constant in the mixtures for which the calculations hold good, then the molecular volume of the water also is constant and the apparent density of the water is $d_w = 1{\cdot}01275$. From this value, the ionic and molecular solution volumes can be obtained, these being presented in the following table, together with values calculated from the ionic lattice radii of Wasastjerna (*loc. cit.*) on the assumption that the ionic volumes bear the same relation to the solution volumes as does the volume of the bivalent oxygen atom O″ (ion) to the water molecule H_2O, taken as 18. The molecular volumes of the acid and salts are taken as the sums of the ionic volumes, the hydrogen ion being assumed to have negligible volume.

	Na˙.	K˙.	Cl′.	H_2O.	HCl.	NaCl.	KCl.
From data	1·58	12·25	22·43	17·795	22·43	24·00	34·66
From lattice radii ...	8·06	17·60	39·83	18·000	39·83	47·89	57·43

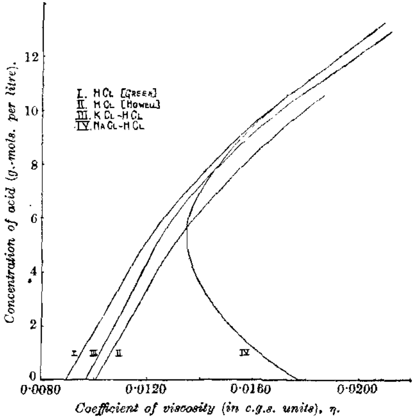
The further removed in size the ion is from the water molecule, the smaller is its apparent solution volume compared with that calculated from lattice radii (compare Hartley and Raikes, *Trans. Faraday Soc.*, 1927, **23**, 393). The values for the acid and salts are roughly half those so derived.

The constancy of the apparent density of the water in the solutions over the ranges indicated is connected with the constancy of the molar concentration of water over these regions, and when the acid concentration rises further, the calculated densities become increasingly lower than the observed values. If the molar or ionic volumes of acid and salt still remain constant, an increase in the apparent density of the water must be assumed.

Thus, to account for the density of the solution for which $a = 7{\cdot}976$ and $b = 0{\cdot}158$ in Table II, the value of K would have to be about 1·0150, and k_1 and k_2 0·0137 and 0·0341, respectively, giving $d_{4°}^{25°}$ (calc.) 1·1296. It would be possible to express the densities of all the solutions of higher acid strength in a similar way. *The changes in the apparent density of water can also be followed in solutions of pure hydrochloric acid, and for this purpose*

the data of Green (J., 1908, **93**, 2023) and Ellis (*J. Amer. Chem. Soc.*, 1916, **38**, 750) have been examined. Calculations based on $d_{4^\circ}^{25^\circ} = 1{\cdot}01275 + 0{\cdot}01375a$ give fair agreement for those regions of acid concentration comparable with the total solute concentrations in the acid–salt mixtures for which the same formula holds, thus indicating that the molecular volumes of water and acid are the same, or nearly so, as in the mixed solutions. There is, however, undoubtedly, a continuous change in the water value as the acid concentration rises from zero.

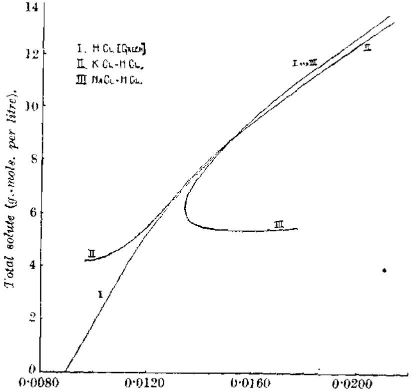
FIG. 2.



Viscosities.—From Tables I and II, it is seen that for the solutions containing potassium chloride the viscosities increase throughout with increasing acid concentration, and that the case for the solutions containing sodium chloride is essentially different, there being a pronounced minimum. In Fig. 2 are plotted the coefficients of viscosity as abscissæ against acid concentration as ordinates. For comparison the curves for the data of Green (*loc. cit.*) at 24·9° and of Howell (J., 1927, 168) at 20° for aqueous solutions of hydrochloric acid alone are also drawn. The positions of the curves in the regions of high acid concentration afford excellent evidence of the accuracy of the method used. The outstanding features of the curves in the regions of medium and low acid concentration are :

first, the parabolic form for the sodium chloride mixtures, and, secondly, the quite different form, similar to that for pure acid solutions, for the potassium chloride mixtures. As shown by Table V, the data for the sodium chloride solutions can be fairly accurately represented by the expression $6700(\eta - \eta_m) = (C - C_m)^2$, where η_m is the minimum viscosity, and C_m the acid concentration of the corresponding solution, η and C being the values for other solutions between $C = 0$ and $C = 10$. Above the latter concentration scarcely any salt is present and the curve is almost linear.

FIG. 3.



Coefficient of viscosity (in c.g.s. units), η.

The interpretation of this relationship is not yet clear and in the meantime another method of approach has been considered.

TABLE V.

$6700 (\eta - \eta_m) = (C - C_m)^2$; $\eta_m = 0{\cdot}01353$; $C_m = 5{\cdot}300$.

C.	η (obs.) $\times 10^5$.	η (calc.). $\times 10^5$.	C.	η (obs.) $\times 10^5$.	η (calc.) $\times 10^5$.
0	1779	1772	4·500	1358	1363
0·503	1694	1696	5·253	1353	1353
0·886	1641	1644	6·101	1357	1363
2·265	1492	1490	7·073	1400	1400
3·185	1419	1420	7·976	1463	1460
3·487	1405	1403	9·236	1582	1584
3·830	1391	1385	13·41	2111	2336

In Fig. 3, the viscosities are plotted against *total solute*, the curve for Green's data again being included. It is now seen that the curve for potassium chloride mixtures lies to the left of that for the pure acid (except at very high concentrations), whilst that for sodium chloride mixtures lies to the right, and solutions of equal chlorine (ion) concentration have in the one case lower and in the other case higher viscosities than for the pure acid solutions. The curves merge at concentrations of about 8·7*N* and above this point those for pure acid and for sodium chloride mixtures are indistinguishable, the concentration of salt being very low; the curve for potassium chloride mixtures in this region diverges from the others, having crossed the pure acid curve at the above point.

Dealing first with the case for the sodium chloride mixtures, for which the volume relations are simpler (since the total number of molecules, water concentration, and chlorine-ion concentration do not vary so much as in the potassium chloride solutions during the replacement of the major portion of the salt by the acid), there has to be explained a large relative fall in viscosity caused by the substitution almost equivalent by equivalent of hydrogen for sodium. The changes are roughly proportional to the fractions of salt precipitated, almost as far as the point of minimum viscosity. The conclusion that the sodium ions are present in the form of particles of relatively large effective size and that they are solvated to a higher degree than the hydrogen ions seems very reasonable.

To obtain an idea of the magnitude of the solvated sodium ions ($Na^{\cdot},xH_2O$), which would quantitatively account for the effects found, the following procedure may be considered.

The formula $\eta_2 = \eta_1(1 + 2{\cdot}5\phi)$ can be applied to calculate the changes of viscosity for hydrochloric acid solutions of from 3·5 to 6*N*, η_1 and η_2 being the viscosities for two different concentrations c_1 and c_2; ϕ is a term $0{\cdot}02243(c_2 - c_1)$, and is therefore the volume of chlorine ions added to 1 c.c. of solution and replacing a volume of water. The volume 22·43 for Cl′ is that already deduced from the density data of these solutions and the mixed solutions. The formula, which is a modification of that of Einstein (*Ann. Physik*, 1906, **19**, 289), gives good agreement when tested on Green's data. Better agreement is, however, obtained by using the formula $\eta_2 - \eta_1 = \frac{1}{2}(\eta_1 + \eta_2) \times 2{\cdot}5\phi$, which expresses the variations about the mean viscosity value in terms of the volumes of ions added or removed, any specific effect of the hydrogen ions being for the present neglected. The formula may now be used to calculate approximately the volume of the sodium ions in a saturated solution of sodium chloride, by comparing this solution with a solution of hydrochloric acid of equal chlorine (ion) concentration, it being

assumed that the hydrated sodium ions have, like the chlorine ions, an effect proportional to their volume. The resulting calculation made from the figures

$$c = 5{\cdot}43\,;\ \eta(\mathrm{NaCl}) = 0{\cdot}01779\,;\ \eta(\mathrm{HCl}) = 0{\cdot}01226, \text{ from graph}$$

gives for the 5·43 g.-ions of sodium in the litre a volume of 147·2 c.c. Hence the volume of ($Na^{\cdot},xH_2O$) is 27·1 c.c. If the value 1·58 found for the $Na^{\cdot}$ ion alone be subtracted, the volume 25·54 c.c. is obtained for the water accompanying 1 g.-ion of sodium, and the hydration number is 1·44, using $d_w = 1{\cdot}01275$.

In a somewhat similar way the series of sodium chloride–hydrochloric acid solutions may be used to obtain the volumes of the $Na^{\cdot},xH_2O$ ions and the hydration numbers, the hydrogen ions being again supposed to have no volume effect. In Table VI are the results of calculations made from values taken from the graphs of the original data, changes of concentration of sodium chloride of 0·5*N* being taken as convenient.

TABLE VI.

η.	NaCl.	HCl.	Total solute.	Vol. of $Na^{\cdot},xH_2O$.	x.
0·01779	5·43	—	5·43	32·02	1·71
0·01713	5·00	0·37	5·37	32·44	1·73
0·01644	4·50	0·86	5·36	31·78	1·70
0·01580	4·00	1·36	5·36	29·26	1·56
0·01525	3·50	1·90	5·40	26·48	1·40
0·01477	3·00	2·42	5·42	29·14	1·55
0·01433	2·50	3·03	5·53	26·32	1·39
0·01396	2·00	3·65	5·65	23·52	1·23
0·01367	1·50	4·30	5·80	32·44	1·73
0·01350	1·00	5·30	6·30		

In these calculations, due allowance has been made for changes of chlorine-ion concentration. It is seen that the degree of hydration (x) of the sodium ions required in order to account for the observed viscosities is quite low, being about 2 for the saturated solution of the pure salt. As acid is added the value falls, and this may be due to the formation of $H_3O^{\cdot}$ ions; but there is at present no direct evidence on this point, although there is evidence that the hydrogen ions are not more highly hydrated. The chlorine ions are probably not appreciably hydrated in these solutions.

The potassium chloride mixtures may now be examined and the hydration numbers derived. In this case we have to deal with the replacement of smaller particles (the potassium ions) by the larger water molecules, the viscosities rising with increasing acid concentration at a greater rate than would be accounted for by the increase in chlorine-ion concentration alone. By comparison of the saturated

potassium chloride solution with the pure acid solution of equal concentration, the calculation for the volume of ions substituted gives, from $c = 4{\cdot}2$, $\eta(KCl) = 0{\cdot}00971$, and $\eta(HCl) = 0{\cdot}01143$, a value 15·5 c.c. for the potassium ion. Since, however, the exchange in this case is not that of H_2O for Cl′, but of K˙ for H_2O, this value really measures the size of a potassium ion compared with a water molecule, as though a water molecule had a volume equal to that of a chlorine ion, and the number requires reducing in the proportion 17·795 : 22·43. If this is done, the final value of 12·29 is obtained, which is almost exactly that previously deduced for the potassium ions from the density data. Hence these ions are not appreciably hydrated.

The series of potassium chloride–acid solutions gives, when examined in this way, as with the sodium chloride series, allowance being made for changes of chlorine-ion concentration, a series of volumes for the potassium ions falling from 15·68 to 12·20, whilst the potassium chloride concentration falls from 4·2 to 0·96, thus supporting the conclusion that the potassium ions do not show hydration to any marked extent. The calculations also further support the view that the chlorine ions are not hydrated, and that there is no hydration of the hydrogen ions beyond the stage $H_3O^{\cdot}$.

It is not suggested that these explanations give a complete account of the phenomena studied. In the regions of higher acid concentration, the viscosities rise much more rapidly than can be accounted for on the basis of the ionic and molar volumes deduced for the lower concentrations, and there are indications of the formation of other types of complex ions.

Summary and Conclusions.

The solubilities have been determined at 25° of potassium and sodium chlorides in aqueous solutions of hydrochloric acid of concentrations varying between 0 and 13·5*N*.

The densities and the viscosities of the same solutions have been measured, the method of Scarpa for the determination of relative viscosity being shown to be trustworthy with the apparatus used.

Complete dissociation of the acid and of the salts being assumed, a formula is developed connecting the densities of the solutions, on the one hand, with the ionic concentrations, ionic solution volumes, and the apparent density of the water in the solutions, on the other; this formula is used for the calculation of the solution volumes of all the constituents. For solutions of acid concentrations between 0 and 6*N*, with either salt, it is unnecessary to assume any variations in the solution volumes and the same values for the chlorine ion and the water molecule apply in both series. These values also give a

satisfactory account of the densities of pure hydrochloric acid solutions of comparable total chloride strength.

Solutions of equal chlorine-ion concentration up to about 9*N* have either lower or higher viscosities than solutions of hydrochloric acid alone according as they are saturated with potassium or with sodium chloride. The solution volumes deduced from the densities are used to give an account of the viscosities of those solutions of hydrochloric acid alone and of potassium chloride–hydrochloric acid to which they refer. No hydration of the chlorine ions is indicated. The potassium ions are hydrated only to a slight extent, if at all. The hydrogen ions may be present in the form $H_3O^{\cdot}$ but are probably not more highly hydrated. The viscosities of the solutions containing sodium chloride cannot be accounted for on a similar basis without introducing a hydration factor of about 2 This value falls as the solutions become more strongly acid.

The author desires to express his thanks to Professor Boon fo providing the facilities which have enabled the work to be carrie out.

HERIOT-WATT COLLEGE, EDINBURGH. [*Received, May 5th*, 1928.]

CCLII.—*The Influence of Structure on the Solubiliti of Ethers. Part I. Aliphatic Ethers.*

By GEORGE MACDONALD BENNETT and WILLIAM GEORGE PHILI

THE mutual solubilities of ethyl ether and water have been dete mined with considerable accuracy by several observers, but t corresponding data for other ethers are lacking. In order to reve the influence of variations in structure on this property, we ha measured the solubilities of six isomeric ethers of the form $C_5H_{12}O$, *viz.*, methyl *n*-butyl, methyl *iso*butyl, methyl *sec.*-but methyl *tert.*-butyl, ethyl *n*-propyl, and ethyl *iso*propyl ethers, a also of the following ethers : methyl *n*- and *iso*-propyl, di-*n*-prop propyl *iso*propyl, di-*n*-butyl, and diallyl.

Preparation of Materials.—With the exception of methyl *te* butyl ether, the ethers were most conveniently prepared by Ch cel's modification (*Annalen*, 1869, **151**, 305) of the William method, in which an alcohol and an alkyl halide are heated w an excess of solid potassium hydroxide. The latter may be hea first under reflux with the alcohol and the halide then added, or other cases, the finely powdered potassium hydroxide may be ad gradually to the boiling mixture of the alcohol and the hal For ethyl *iso*propyl ether, ethyl iodide, *iso*propyl alcohol,

potassium hydroxide were heated in a closed bottle at 100° for several hours. It was found necessary to use only normal alkyl iodides in this reaction, methyl *iso*propyl ether being obtainable, for example, from *iso*propyl alcohol and methyl iodide, but not from methyl alcohol and *iso*propyl iodide. Methyl *tert.*-butyl ether could not be prepared by Chancel's method, and that of Henry (*Rec. trav. chim.*, 1904, **23**, 329) was adopted.

The customary methods of purification of some of these substances were incapable of removing the last traces of the halides used in their preparation. A specimen of ethyl *iso*propyl ether, for instance, after repeated fractional distillation and after boiling for 6 hours with metallic potassium, still contained some iodide, although its density, $d_{4^\circ}^{0^\circ}$ (vac.) 0·7452, was in agreement with the value in the literature. (Compare the difficulty of removing iodides from hydrocarbons; Welt, *Compt. rend.*, 1894, **119**, 743.) The trace of iodide was completely removed by boiling the liquid for 5 hours with diethylamine (15—20% by wt.), and then washing it successively with water, dilute acid, and again with water. The specimen, referred to above, thus purified had, after drying and redistillation, $d_{4^\circ}^{0^\circ}$ (vac.) 0·7440; it was entirely free from halogen, and a repetition of the process of purification caused no further alteration in its density. This method of purification was applied in all cases where an alkyl halide had been used, and the ethers were obtained in a state of greater purity than had previously been attained, as is shown by the fact that the densities observed are in several cases lower than those recorded in the literature.

The following constants were observed (all densities are reduced to a vacuum; the b. p.'s are corrected, but are not to be regarded as such trustworthy criteria of purity as the densities, since often only small quantities of material were available): Methyl *n*-butyl ether, b. p. 70°, $d_{4^\circ}^{0^\circ}$ 0·7635, $d_{4^\circ}^{20^\circ}$ 0·7441; methyl *iso*butyl ether, b. p. 58°, $d_{4^\circ}^{0^\circ}$ 0·7523, $d_{4^\circ}^{20^\circ}$ 0·7311; *methyl sec.-butyl ether*, prepared by Chancel's method and purified as described above, b. p. 59°, $d_{4^\circ}^{0^\circ}$ 0·7621, $d_{4^\circ}^{20^\circ}$ 0·7415 (Found: C, 68·8; H, 13·8. $C_5H_{12}O$ requires C, 68·3; H, 13·6%); methyl *tert.*-butyl ether, b. p. 54°, $d_{4^\circ}^{20^\circ}$ 0·7578; ethyl *n*-propyl ether, b. p. 64°, $d_{4^\circ}^{0^\circ}$ 0·7541, $d_{4^\circ}^{20^\circ}$ 0·7330; ethyl *iso*propyl ether, b. p. 53°, $d_{4^\circ}^{0^\circ}$ 0·7440, $d_{4^\circ}^{20^\circ}$ 0·7211; methyl *n*-propyl ether, b. p. 37°, $d_{4^\circ}^{0^\circ}$ 0·7494, $d_{4^\circ}^{13 \cdot 0^\circ}$ 0·7356; methyl *iso*propyl ether, b. p. 32°, $d_{4^\circ}^{0^\circ}$ 0·7383, $d_{4^\circ}^{15^\circ}$ 0·7237; di-*n*-propyl ether, b. p. 91°, $d_{4^\circ}^{20^\circ}$ 0·7360; *n*-propyl *iso*propyl ether, b. p. 83°, $d_{4^\circ}^{0^\circ}$ 0·7597, $d_{4^\circ}^{12 \cdot 5^\circ}$ 0·7474; di-*n*-butyl ether (purchased), b. p. 140°, $d_{4^\circ}^{0^\circ}$ 0·7841; diallyl ether, b. p. 94°, $d_{4^\circ}^{0^\circ}$ 0·8449, $d_{4^\circ}^{20^\circ}$ 0·8260.

Methods of Measurement.—Of the methods available for determining the mutual solubilities of two liquids, that of Hill (*J. Amer.*

Chem. Soc., 1923, **45**, 1143) appeared to be the best, particularly as it gives information as to the composition of both phases of the system; as originally described, however, it involved large vessels and the use of at least 400 c.c. of each liquid, and we therefore reduced the scale of the apparatus in order to adapt it to small quantities of substances (*i.e.*, 4—5 c.c. of each liquid) without appreciable loss of accuracy. The two vessels (Fig. 1) were made from glass tubing of 5 mm. bore, graduated in mm., and were care-

FIG. 1.

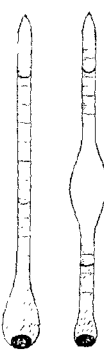
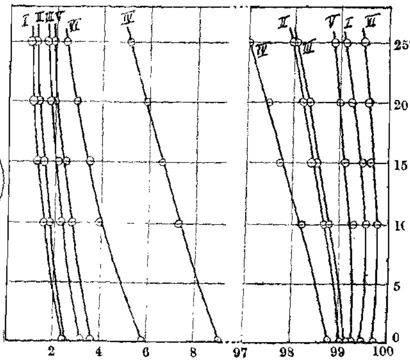


FIG. 2.



Weight of ether, %.

Mutual solubilities of isomeric ethers $C_5H_{12}O$ *and water.*

I. *Methyl* n-*butyl ether.*
II. *Methyl* iso*butyl ether.*
III. *Methyl* sec.-*butyl ether.*
IV. *Methyl* tert.-*butyl ethe*
V. *Ethyl* n-*propyl ether.*
VI. *Ethyl* iso*propyl ether.*

fully calibrated (in the thermostat) by measuring the volumes observed weights of pure toluene. The pear-shaped form of t bulbs is important in order to allow the two phases to segrega completely.

It was at first found difficult to secure complete mixing of t phases in these narrow tubes in which an air bubble would r travel. An electromagnetically activated plunger did not bri about rapid mixing, but excellent results were obtained by enclos in the tube a globule of pure mercury occupying about 1 cm. of narrow part. When the tube was repeatedly inverted in the th

mostat, the mercury travelled down the tube and caused turbulent mixing, complete equilibrium being reached in less than ½ hour.

The thermostat was electrically heated and controlled, the variation being less than 0·01°. Temperatures were read on a thermometer graduated in 0·1° and recently standardised at the National Physical Laboratory. When mixing had been effected, the tubes were attached to a frame and rotated about a vertical axis for 10 minutes to promote the separation of the phases. The tubes were then fixed, preparatory to reading the volumes, in such a position that the glass points, where they had been sealed in filling, protruded 1 cm. above the water in the bath, and a current of hot air was blown on to the tips to drive down any liquid into the body of the tube. The volumes of the phases were then read through a telescope 3 feet from the glass front of the thermostat, strong illumination being supplied through a ground glass screen behind the tubes. The mixing and manipulations were repeated until the readings were constant, the values in practice being reproducible to less than 0·01 c.c. The possibility of error due to the difference in shape of the ether–water and ether–air menisouses was examined by a trial with pure paraffin (b. p. 60—70°) and water. Any error involved is less than that of observation.

A redetermination of the solubilities of ethyl ether at several temperatures gave the following results :

Temp.	Ether in aqueous phase.	Water in ether phase.
25°	6·03% (6·03)	1·30% (1·34)
20	6·87 (6·90)	1·24 (1·26)
15	7·95 (7·91)	1·26 (1·24)
10	9·01 (9·04)	1·14 (1·16)

The agreement with Hill's values (in brackets) is close, and there is reason to believe that the reduction of scale of the experiments has not introduced an error as large as 0·05%. Apart from this, our figures are presumably subject to a small error inherent in the original method when very low solubilities are measured (compare Kablukov and Malischeva, *J. Amer. Chem. Soc.*, 1925, **47**, 1553; Hill and Malisoff, *ibid.*, 1926, **48**, 918). This error is not large, and, being systematic, will not affect the validity of any comparison made between similar values of solubility. We obtained an indication of some error of this kind by comparing the figures for *n*-propyl ether, obtained by the method described above, with those found by the "synthetic" method of Alexejew (*Wied. Ann.*, 1886, **28**, 305). In this case the latter figures are consistently 0·2% lower than the former. For a few of the ethers examined, determinations were made by the synthetic method and for the aqueous phase only. Weighed quantities of the ether and of water were sealed up together,

and the temperature at which turbidity just appeared was determined in a large vessel of water.

TABLE I.

A = weight % of ether in aqueous phase. B = weight % of water in ether phase.

Ether.		25°.	20°.	15°.	10°.	0°.
Methyl *n*-butyl	A	0·89	1·00	1·18	1·51	2·51
Q + 6800 cals.	B	0·91	0·71	0·57	0·45	0·50
Methyl *iso*butyl	A	1·10	1·24	1·51	1·79	2·53
Q + 6050 cals.	B	2·02	1·78	1·54	1·30	0·92
Methyl *sec.*-butyl	A	1·60	1·79	2·05	2·33	3·24
Q + 4350 cals.	B	1·95	1·69	1·48	1·22	0·80
Methyl *tert.*-butyl	A	5·16	5·83	6·55	7·30	9·12
Q + 3700 cals.	B	2·95	2·54	2·20	1·84	1·17
Ethyl *n*-propyl	A	1·87	2·03	2·32	2·74	3·66
Q + 4950 cals.	B	1·13	1·01	0·88	0·76	0·69
Ethyl *iso*propyl	A	2·40	2·82	3·35	3·99	5·89
Q + 5700 cals.	B	0·52	0·41	0·30	0·22	0·26
Diallyl	A	8·86	9·18	9·61	10·20	11·68
Q + 1750 cals.	B	1·51	1·25	1·05	0·91	0·71
Di-*n*-propyl	A	0·49	0·54	0·61	0·71	1·05
	B	0·46	0·38	0·31	0·29	0·36

TABLE II.

Weights % of ether in water.

Ether.	25°.	20°.	15°.	10°.	0°.
Di-*n*-propyl	0·25	0·30	0·38	0·41	0·58
n-Propyl *iso*propyl ...	0·47	0·51	0·60	0·75	—
Methyl *n*-propyl	3·05	3·2	3·4	3·8	5·6
Methyl *iso*propyl	6·5	7·4	8·6	9·7	—
Di-*n*-butyl	Solubility less than 0·01% at 17° (2 litres of water did not completely dissolve 0·2 g.).				

Results.—Measurements by the volumetric method were made at 25°, 20°, 15°, 10°, and 0·25° or 0·5°. Two separate sets of measurements were made in each case. The resulting data for the isomeric ethers $C_5H_{12}O$ are plotted in Fig. 2, the scale being doubled for the right-hand curves for the sake of clearness. The values recorded in Table I have been taken from the smooth curves : the corrections thus introduced are usually of the order ± 0—0·05%. The curves in Fig. 3, except those of ethyl and allyl ethers, record measurements by the synthetic method, and the smoothed values are given in Table II.

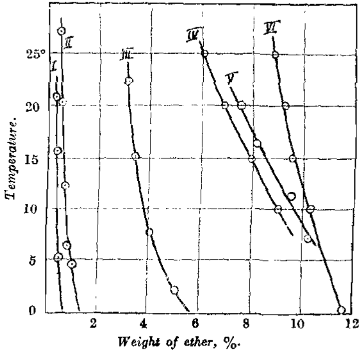
Discussion of Results.

The solubilities of water in the ethers are all small, and vary very little with temperature. Those of the ethers in water vary over a wide range for the isomeric substances studied. These values, moreover, all decrease with rising temperature. Approximate

values of the (positive) molecular heats of solution (Q) of the ethers in water have been calculated in the usual way from the slopes of the solubility curves at 10—20° and are recorded in Table I.

It is noticeable that the relative order of the solubilities of the compounds remains the same at all temperatures. For the isomeric ethers $C_5H_{12}O$, this order is: Methyl *n*-butyl (1·51), methyl *iso*butyl (1·79), methyl *sec.*-butyl (2·33), ethyl *n*-propyl (2·74), ethyl *iso*propyl (3·99), methyl *tert.*-butyl (7·30), the figures in brackets being the values at 10°. The order for the isomerides $C_4H_{10}O$ is:

FIG. 3.



Solubilities in water of:

I. *Di-n-propyl ether.*
II. *Propyl isopropyl ether.*
III. *Methyl n-propyl ether.*
IV. *Diethyl ether.*
V. *Methyl isopropyl ether.*
VI. *Diallyl ether.*

lethyl *n*-propyl (3·8), diethyl (9·0), and methyl *iso*propyl (9·7). Throughout these values the solubility is seen to increase with ncreased branching of the carbon chains of the alkyl groups.

The various physical properties of ethers in the pure state how them to be correctly classified as "normal" liquids. Evidence of various kinds is available in the case of ethyl ther: surface tension data are given by Morgan and Stone (*J. Amer. Chem. Soc.*, 1913, **35**, 1505) showing the same result with thyl *n*-propyl ether, and measurements of the solubility of naphthaene in some of these ethers, which lead to the same conclusion, are ecorded in Part II of this investigation; but the considerable

solubility of the ethers in water indicates "abnormal" behaviour, and classifies them as "polar" in the sense suggested by G. N. Lewis (*ibid.*, p. 1448). This abnormality, absent in the pure liquid but developed in presence of water, is evidence of the presence in the latter case of a new molecular species of a polar type. Moreover, the comparative solubilities may be taken as an approximate indication of variations in the extent of the chemical action to form the complex $R_2O \longrightarrow HOH$. This point of view has recently been clearly stated by Sidgwick (Presidential Address to the British Association, Section B, 1927, and "The Electronic Theory of Valency," p. 137), who also explains the abnormally high solubilities in ether of hydroxylic substances in general as due to combination of the two to give the polar compound $R_2O \longrightarrow HOR$.

Three factors might consequently be expected to influence the solubilities in water of ethers which are of the same molecular weight.

(*a*) The chemical reactivity of the oxygen atom might be lowered by any accumulation of groups in its vicinity. Such a steric hindrance should cause a diminution in the solubility of isomerides as a normal radical is replaced by a secondary or tertiary one.

(*b*) The donating properties of the oxygen atom should, on the other hand, be increased if the attached radicals have an increased tendency to repel electrons (the "electron-source" effect). The experiments of Allan, Oxford, Robinson, and Smith (*J.*, 1926, 401) have shown that the methyl group and particularly secondary alkyl radicals have this type of influence on a contiguous oxygen atom, as shown by its activity in controlling aromatic substitution. For this reason, therefore, the attachment of a secondary or tertiary radical to the oxygen of an ether should cause an increased solubility in water. An effect of this kind is somewhat similar to that which results in the higher strength of secondary aliphatic bases as compared with primary bases.

(*c*) Any increase in the length of a hydrocarbon chain will tend to reduce the solubility in water of the ether or of its complex with water (compare Langmuir, *Colloid Symposium Monograph*, Vol. 3, Chem. Catalog. Co., New York, 1925). It should be noticed that this effect is purely negative. The substitution of the *tert.*-butyl for the *n*-butyl radical does not, in the absence of an oxygen atom, confer an appreciable solubility on a substance, for *n*- and *iso*-butane are equally sparingly soluble in water.

The steric hindrance effect (*a*) appears to have been demonstrated for certain complexes of the alcohols by the experiments of Tschelinzeff (*Bull. Soc. chim.*, 1924, **35**, 741), but our figures do not reveal it. It is possible that this influence is present, but of a lower order of magnitude than the other effects, which oppose it. To

the latter effects, (*b*) and (*c*), may be attributed the observed variations of solubility. Although in general these two influences cannot be observed separately, the increased solubility of $MeO{\cdot}CH_2{\cdot}CHMe_2$ as compared with $MeO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Me$ does presumably depend entirely on the length of hydrocarbon chain (*c*), whilst the increased value for $MeO{\cdot}CHMe{\cdot}CH_2Me$ as compared with $MeO{\cdot}CH_2{\cdot}CHMe_2$ reveals factor (*b*) independently of (*c*). The rapid fall in solubility with lengthened hydrocarbon chain, when molecular weight does not remain constant, is well shown by the following ethers: Ethyl (9·0), ethyl *n*-propyl (2·74), dipropyl (0·41), dibutyl (<0·01). In the molecule of diallyl ether the unsaturated groups confer a considerable freedom of movement of electrons, which should assist the donating function of the oxygen atom. The relatively high solubility of this substance was therefore to be expected.

THE UNIVERSITY, SHEFFIELD. [*Received, June 7th, 1928.*]

CCLIII.—*The Influence of Structure on the Solubilities of Ethers. Part II. Some Cyclic Ethers.*

By GEORGE MACDONALD BENNETT and WILLIAM GEORGE PHILIP.

A SERIES of cyclic ethers has been examined with respect to the solubilities in water, the compounds (*a*) being isomeric, (*b*) differing from the series of open-chain ethers (preceding paper) only by two hydrogen atoms and the closure of the ring, and (*c*) having a cyclic structure with a 6-, 5-, 4-, or 3-membered ring. The substances chosen were pentamethylene oxide, α- and β-methyltetramethylene oxides, *ββ'-dimethyltrimethylene oxide, αα'-dimethyltrimethylene oxide*, and αα'-methylethylethylene oxide, all of the molecular formula $C_5H_{10}O$.

Preparation of Materials.—(i) Pentamethylene oxide was prepared as described by Clarke (J., 1912, **101**, 1788), and had b. p. 87°, $d_{4^\circ}^{20^\circ}$ (vac.) 0·8814.

(ii) α-Methyltetramethylene oxide was obtained from the glycol resulting from the reduction of γ-acetylpropyl alcohol. The yields of the latter were consistently lower than those claimed by Possaner and von Ehrenthal (*Monatsh.*, 1903, **24**, 352): substitution of ethylene chlorobromide for ethylene dibromide caused no improvement, but the following method involving the use of ethylene chlorohydrin was much more satisfactory. To a solution of ethyl acetoacetate (65 g.) with sodium (12 g.) in ethyl alcohol (130 g.), ethylene chlorohydrin (45 g.) was added and the mixture boiled for 5 hours. The solution was filtered, evaporated, and the residue

boiled for 5 hours with dilute hydrochloric acid (120 c.c.; 10%). The solution was made neutral and concentrated under reduced pressure until salt had separated copiously. An excess of acetone was then added, the solution filtered from salt, evaporated, and distilled under reduced pressure (yield, 40%). The ether had b. p. 80°, $d_{4^\circ}^{0^\circ}$ (vac.) 0·8732, $d_{4^\circ}^{20^\circ}$ (vac.) 0·8540.

(iii) β-Methyltetramethylene oxide was prepared from ethyl methylsuccinate as described by Harries (*Annalen*, 1911, **383**, 170), and had b. p. 83°/738 mm., $d_{4^\circ}^{0^\circ}$ (vac.) 0·8850, $d_{4^\circ}^{20^\circ}$ (vac.) 0·8642.

(iv) ββ'-*Dimethyltrimethylene oxide* was made from the corresponding glycol (Just, *Monatsh.*, 1896, **17**, 76) through its monobromohydrin (Franke, *ibid.*, 1913, **34**, 1898). An improved yield of the latter was furnished by heating the glycol (1 mol.) with the solution made by passing sulphur dioxide into bromine (100 g.) and ice (110 g.) until the colour is yellow. The mixture was heated on the steam-bath for 5 hours, at its boiling point for 1 hour, and then diluted. The product was extracted in ether, the extract washed with sodium carbonate solution, dried over sodium sulphate, and fractionated. The bromohydrin had b. p. 100°/25 mm. (yield, 41%). It was mixed with three times its weight of dry, powdered potassium hydroxide, and heated in an oil-bath at 130—180°. The ββ'-dimethyltrimethylene oxide, after drying and redistillation, was a mobile liquid of camphoraceous odour, b. p. 78°/742 mm., $d_{4^\circ}^{0^\circ}$ (vac.) 0·8550, $d_{4^\circ}^{20^\circ}$ (vac.) 0·8348 (Found: C, 69·1; H, 11·5. $C_5H_{10}O$ requires C, 69·8; H, 11·6%).

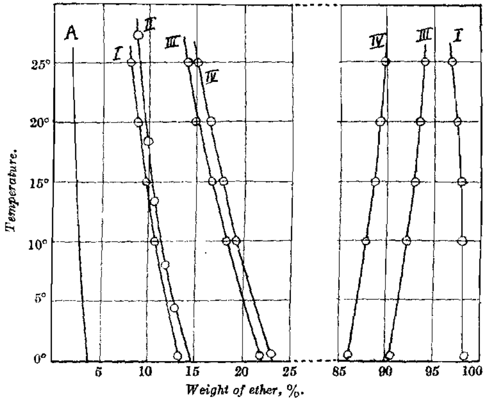
(v) αα'-*Dimethyltrimethylene oxide* was prepared in a similar manner (yield, 43%) from the chlorohydrin, b. p. 72°/13 mm., obtained by the action of magnesium methyl iodide on ethyl β-chloropropionate (yield, 53%) as described by Henry (*Compt. rend.*, 1906, **142**, 133). The *oxide* had b. p. 71°/750 mm., $d_{4^\circ}^{0^\circ}$ (vac.) 0·8490, $d_{4^\circ}^{20^\circ}$ (vac.) 0·8279. It is a liquid of pleasant odour, and dissolves with evolution of heat in water, becoming hydrated to the corresponding glycol. Great difficulty was experienced in analysing this and the foregoing substance: apart from their volatility, the *gem*-dimethyl group may have caused low values. This substance was also hygroscopic. The specimens were always redistilled immediately before use, but no direct evidence of their freedom from impurity is available.

(vi) αα'-Methylethylethylene oxide was prepared as described by Tiffeneau (*Compt. rend.*, 1902, **134**, 775; 1907, **145**, 437). It had b. p. 80·5°/755 mm., $d_{4^\circ}^{0^\circ}$ (vac.) 0·8425, $d_{4^\circ}^{20^\circ}$ (vac.) 0·8220 (Found: C, 70·2; H, 11·4. Calc.: C, 69·8; H, 11·6%).

Methods of Measurement.—The experimental method was as described in the preceding paper. The solubilities of β-methyl-

tetramethylene oxide were determined by the synthetic method. With this, and with one or two other substances, a difficulty was sometimes met with in using the volumetric method described. A trace of a solid was produced in the tubes which made the separation of the phases and the reading of the meniscus difficult. The effect was slight and in some cases entirely absent. It was found by repeated experiment to be unconnected with any possible impurity in the mercury, and was finally recognised as due to the

Fig. 1.



Mutual solubilities of isomeric cyclic ethers and water.

I. *Pentamethylene oxide.* III. *a-Methyltetramethylene oxide.*
II. *β-Methyltetramethylene oxide.* IV. *ββ'-Dimethyltrimethylene oxide.*
(A, *Ethyl* n-*propyl ether.*)

›xidation of the metal to an oxide by a trace of ether peroxide compare Richardson, J., 1891, **59**, 51). The moist ether is thus catalyst which causes reaction between mercury and oxygen. If his explanation had heen realised originally, the whole phenomenon ould doubtless have been suppressed by avoiding the presence of xygen. The measurements here recorded are free from errors due o this difficulty, but the alternative method of measurement was dopted for the one ether.

As a check on the behaviour of these substances in the pure tate, the solubilities of naphthalene in them and in three open-

chain ethers at several temperatures were determined, following the method of Ward (*J. Physical Chem.*, 1926, **30**, 1316). The naphthalene was carefully purified and melted completely between 80·05° and 80·07°.

Results.—The mutual solubilities of four cyclic ethers and water are shown by the curves in Fig. 1, a curve for ethyl *n*-propyl ether being included for comparison. The data in Table I are smoothed values for these substances. The remaining two ethers, αα'-dimethyltrimethylene oxide and αα'-methylethylethylene oxide, dissolve completely in water with considerable evolution of heat. The resulting solutions were found to contain only the corresponding glycols, and these two ethers could not be recovered.

TABLE I.

Mutual solubilities of cyclic ethers and water.

A = weight % of ether in aqueous phase. B = weight % of water in ether phase.

Oxide.		25°.	20°.	15°.	10°.	0°.
Pentamethylene	A	8·02	8·76	9·64	10·70	13·40
Q + 3300 cals.	B	3·14	2·70	2·27	2·08	1·63
α-Methyltetramethylene	A	13·87	15·05	16·52	18·20	22·10
Q + 3150 cals.	B	6·08	6·65	7·05	7·72	9·54
β-Methyltetramethylene	A	8·8	9·5	10·2	11·25	14·6
Q + 2800 cals.						
ββ'-Dimethyltrimethylene	A	15·04	16·26	17·71	19·31	23·28
Q + 2800 cals.	B	10·20	10·67	11·32	12·15	13·96

TABLE II.

Solubilities of naphthalene in open-chain and in cyclic ethers.

(t = temperature; N = molar fraction of naphthalene.)

Di-*n*-butyl ether	t	42·6°	45·7°	52·9°
	N	0·3773	0·4153	0·5078
Ethyl *n*-propyl ether	t	29·9°	39·7°	42·3°
	N	0·2708	0·3650	0·3930
Ethyl *iso*propyl ether	t		43·9°	52·3°
	N		0·4026	0·5136
Pentamethylene oxide	t	28·4°	30·1°	40·2°
	N	0·3421	0·3705	0·4608
ββ'-Dimethyltrimethylene oxide	t	29·2°	38·9°	
	N	0·3460	0·4173	
αα'-Dimethyltrimethylene oxide	t	33·8°	39·9°	44·7°
	N	0·3010	0·4087	0·4557
αα'-Methylethylethylene oxide	t	27·4°	38·2°	46·6°
	N	0·3256	0·4223	0·5052

Discussion of Results.

The deviation of the solubilities of naphthalene in the ethers from the ideal value may be shown by the slope of the curve relating

log N to $1/T$ (Mortimer, *J. Amer. Chem. Soc.*, 1922, **44**, 1416; 1923, **45**, 633). The mean values of $\Delta \log N/\Delta(1/T)$ derived from the data in Table II are: Dibutyl ether 1245, ethyl *n*-propyl ether 1190, ethyl *iso*propyl ether 1200, pentamethylene oxide 920, ββ′-dimethyltrimethylene oxide 980, αα′-dimethyltrimethylene oxide 1120, αα′-methylethylethylene oxide 985. The ideal value may be taken to be 970, and the value recorded by Mortimer for ethyl ether is 1180. The figures show tbat these liquids are normal and differ very little in internal pressure from naphthalene, the cyclic oxides having a slightly higher internal pressure than the others. The figures for the last two ethers in the above list are possibly subject to error owing to the hygroscopic nature of the substances. The observed points for the cyclic ethers are close to the ideal curve, and the internal pressures may be taken to be approximately equal to that of naphthalene (1·00 on Mortimer's scale). This slightly greater internal pressure is also apparent from a consideration of the following boiling points: *n*-Hexane 69°, *cyclo*hexane 81°, ethyl *n*-propyl ether 64°, methyl *n*-butyl ether 70°, pentametbylene oxide 87°.

The solubilities of the cyclic ethers in water increase with falling temperature, but their relative order is independent of this change. The solubilities are in tbe order: Ethyl *n*-propyl ether (2·74), pentamethylene oxide (10·70), β-methyltetramethylene oxide (11·25), α-methyltetramethylene oxide (18·20), ββ′-dimethyltrimethylene oxide (19·31), the figures in brackets being the solubilities at 10·0°.

The difference between the solubilities of α- and β-methyltetramethylene oxides once more illustrates the effect of substituting a secondary for a primary radical attached to the oxygen atom, as discussed in Part I of this investigation. The extreme development of chemical reactivity due to a tertiary radical is seen in αα′-dimethyltrimethylene oxide and αα′-methylethylethylene oxide by the immediate rupture of the ring on solution in water.

The most striking feature of the results is the large increase of solubility caused by the closure of the ring, and this is also true of the solubilities of water in the ethers, the values of which are considerable.

The work of Menschutkin (J., 1906, **89**, 1532) and of Petrenko-Kritschenko (*Annalen*, 1905, **341**, 165) proved that the reactivity of an alcohol or a ketone is increased when its open chain is closed into a ring. If the open-chain substance be regarded as behaving normally, ring closure evidently confers an enhanced reactivity. This effect, which is of the nature of a negative steric hindrance, may be termed "steric activation." Menschutkin realised that this phenomenon should also arise in the closing of a heterocyclic

ing, and cited as an illustration the greater velocity of alkylation of piperidine than of *n*-amylamine. The much greater strength of piperidine as a base in comparison with diethylamine and dipropylamine may also be ascribed to steric activation. The measurements recorded in this paper are evidence of a similar effect with oxygen as the hetero-atom. To show that the solubility developed by closure of the ring is a property of the oxygen atom in particular, the solubilities of *n*-hexane and *cyclo*hexane in water were examined. Direct experiment showed that water dissolves less than 0·005% of either at 17°.

The increase of solubility due to the closure of the ring is also larger the smaller the ring, in accordance with expectation. Considering only the ethers with unsubstituted methylene groups attached to the oxygen atom, the figures to be compared are 10·70, 11·25, and 19·31% for 6-, 5-, and 4-membered rings, respectively. The fact that the difference between the first two is small is perhaps due to the strainless configuration in the 6-membered ring, which will consequently have a similar angle to that of its 5-membered isomeride. The observation of Bergmann and Kann (*Annalen*, 1924, **438**, 278), that acetoxypolymethylene oxides of the type $R\cdot\overset{\ulcorner\!\!-\!-\!-O-\!-\!-\!\!\urcorner}{CH\cdot(CH_2)_n\cdot CH}\cdot OAc$ are polymerised to a greater extent the smaller the value of n, is evidence of a similar increase of chemical reactivity in the oxygen atom with diminishing size of the ring.

It may also be pointed out that the large majority of stable oxonium compounds arise from the chemical reactivity of an oxygen atom which is a member of a ring. This can hardly be accidental, but must be a consequence of the steric activation of such atoms.

We are indebted to the Department of Scientific and Industrial Research for a grant which enabled one of us to take part in the work recorded in this and the preceding paper.

THE UNIVERSITY, SHEFFIELD. [*Received, June 7th*, 1928.]

CCLIV. *The Phosphorescent Combustion of Sulphur.*

By HARRY JULIUS EMELÉUS.

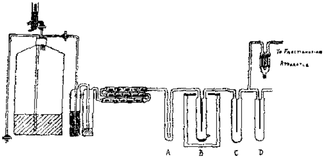
THE temperature at which sulphur ignites in oxygen varies between 285° and 325° according to the conditions (Moissan, *Compt. rend.*, 1903, **137**, 547). Just below the ignition point the oxidation is accompanied by a bluish-white luminescence (Joubert, *ibid.*, 1874, **78**, 1853) persisting only so long as heat is supplied; at lower temperatures the reaction is non-luminous. The phosphorescent flame changes

into the normal flame as the temperature is raised. Heumann showed that its products were sulphur dioxide and a little sulphur trioxide (*Ber.*, 1883, **16**, 139). Bloch found that no ionisation occurred, but stated (without giving details of his experiments) that ozone was formed (*Compt. rend.*, 1909, **148**, 782). The phosphorescent flame was also investigated by Watson (*Chem. News*, 1913, **108**, 187). The main aim of the present investigation was to search for any oxide of sulphur more volatile than sulphur dioxide (such as the still unknown sulphur monoxide might be expected to be), by methods which would enable a very small percentage of such a substance to be isolated. The alleged formation of ozone and the action of inhibiting substances on the phosphorescent flame were also examined.

The Products of the Phosphorescent Combustion of Sulphur.

The production and maintenance of the phosphorescent flame was most readily accomplished by using mixtures of oxygen and

FIG. 1.



nitrogen (obtained from cylinders) with an oxygen content varying between 5—15%, according to the temperature at which the flame was being maintained. All tendency for normal burning to occur was eliminated in this way. The apparatus used for collecting the oxidation product is shown in Fig. 1. The gas mixture from the storage bottle was passed over soda-lime and dried by sulphuric acid and phosphoric oxide, residual condensable impurities being then removed in the U-tube *A* cooled in liquid air. Recrystallised sulphur (Merck's), which had been maintained in a vacuum at its melting point for ½ hour to remove solvent, distilled in a vacuum, and broken up, was distilled in a vacuum directly into *B* from a side tube, before the apparatus was assembled. *B* was heated in an electric furnace (10 cm. internal diameter), temperatures being recorded by a mercury thermometer in contact with the outside of the bulb. The flame in a gas stream under these conditions was invisible, except in a dark room, and remained steady over long periods. Its temperature was approximately 5° above that of the

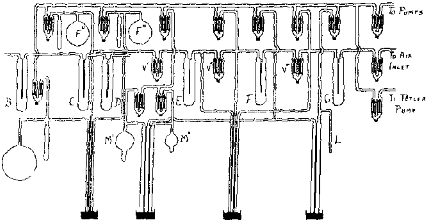
furnace. The oxidation product was frozen in *C*, which was cooled in liquid air, and it is assumed that none of the product escaped condensation under such conditions. The guard-tube *D* was similarly cooled. Connexion was made between *C* and *D* to an apparatus for the subsequent examination of the oxidation product.

Combustion was always incomplete, as shown by the following values for the oxygen content of the gas issuing at *D* for various temperatures of *B*. The ingoing gas contained 8·2% of oxygen, and was passed at the approximate rate of 1 l. per hour.

Oxygen in outgoing gas, %	7·6	5·8	5·2
Temperature	257°	326°	350°

After a number of trials, three experiments were carried out at 275°, 300°, and 325° respectively. The oxidation product

FIG. 2.



condensed in *C* was examined by a process of fractionation in the apparatus shown in Fig. 2 (compare Stock, *Ber.*, 1914, **47**, 154; 1917, **50**, 989; 1918, **51**, 983). *C* being cooled in liquid air, *B* and *D* were sealed off, the mercury valve *V'* (Stock, *Z. Elektrochem.*, 1917, **23**, 33) was opened, and the whole apparatus evacuated with a single-stage quartz diffusion pump, backed by a Cenco Hyvac pump. All the valves except *V'*, *V''*, and *V'''* were then closed, and the U-tubes *E*, *F*, and *G* were cooled in baths at −85°, −124°, and in liquid air respectively; *C* was then allowed to warm slowly to room temperature. Its contents thus underwent a process of fractional condensation in *E*, *F*, and *G* (time, 20 minutes); the valves *V''* and *V'''* were closed, and the residual solid in *C* was sublimed into *E*, which was cooled in liquid air, *V'* being then closed.

Examination of the Volatile Product.—The condensate in *G* (which was always very small) was distilled into *L* (of known volume), where its volume was determined by allowing it to vaporise and

observing the pressure produced at a known temperature; the vapour pressure at a suitable temperature was also determined. It was then distilled back into *G* and stored. The condensate in *F* was divided into three fractions in order of descreasing volatility by allowing evaporation to occur at $-56°$ to $-58°$. The volume of each of these in turn was determined in the gas measuring flask M'', of known volume, and the vapour pressure–temperature curve of each was determined in *L*, after which the fractions were stored in M', F'', and F'''.

Results.

(All recorded gas volumes are reduced to 0° and 760 mm. of mercury.)

Experiment 1. Temperature, 275° (± 3°). Approximately 17 l. of an oxygen–nitrogen mixture containing 13·7% of oxygen were passed at the rate of 1 l. per hour.

Fraction in G : Volume = 0·1 c.c.; vapour tension at 99° = 0·7 mm.

Fraction in F :

Most volatile fraction. (Volume = 41·7 c.c.)		Middle fraction. (Volume = 58·5 c.c.)		Least volatile fraction. (Volume = 91·6 c.c.)	
Temp.	Vap. press.	Temp.	Vap. press.	Temp.	Vap. press.
−57·6°	38·0 mm.	−56·4°	41 mm.	−72·6°	10·5 mm.
−47·2	77·0 ,,	−48·3	70 ,,	−54·6	44 ,,
−37·1	151 ,,	−38·0	144 ,,	−40·0	123 ,,
−27·7	266 ,,	−28·2	260 ,,	−27·9	259 ,,
−17·6	470 ,,	−16·9	484 ,,	−17·5	459 ,,

The small fraction in *G* had a vapour tension consistent with its being sulphur dioxide which had escaped condensation in *F*. Any more volatile oxidation product would have collected in *G*, and its absence is a conclusive proof that no such product is formed in the phosphorescent flame. The experiment would not, however, have detected any substance not condensed in liquid air. It was shown in a separate experiment that no substance more volatile than sulphur dioxide and reacting with mercury was present.

The above vapour-tension measurements for the three fractions obtained from the condensate in *F* fall on one curve, indicating that a homogeneous substance was present. They agree with the values for pure sulphur dioxide obtained by use of the same pentane-filled thermometers, showing the condensate to be pure sulphur dioxide. The experiments at 300° and 325° were carried out in precisely the same manner, and led to the same conclusions. Unless special precautions were taken to avoid contamination of the sulphur by dust, a small quantity of carbon dioxide (varying from 0·6 c.c. to 0·2 c.c.) was formed during the oxidation, and was readily isolated

from the condensate in *G*, and identified by vapour-tension measurements.

The less volatile reaction product. A small quantity of solid was always found in *C* and *E*. In some experiments it was white, but in others it contained a deep blue material which disappeared after 48 hours and was not isolated. Its colour and behaviour suggested that it was sulphur sesquioxide. Its formation always occurred where solid sulphur dioxide had melted in the condensing tube, and was most pronounced at higher temperatures and with faster gas streams—two conditions favouring the sublimation of sulphur. It is concluded that this lower oxide was produced in a secondary reaction between sulphur trioxide (see below) and sulphur.

The white reaction product dissolved in water, giving a fog, and the solution contained sulphuric acid and was without reducing properties on indigo solution. It appeared to be sulphur trioxide, confirming an observation by Heumann (*loc. cit.*). Its vapour attacked mercury, giving sulphur dioxide and a sulphate. In the experiment at 275° already described, 2·2 c.c. of sulphur dioxide were formed in this way. Assuming an equal quantity of sulphur to have combined with the mercury, the quantity of sulphur trioxide formed in the phosphorescent combustion was approximately 2% of the quantity of sulphur dioxide. The value given for the formation of the trioxide in the normal combustion is approximately the same (Hempel, *Ber.*, 1890, **23**, 1455).

Formation of Ozone in the Phosphorescent Flame of Sulphur.—At the temperature at which sulphur glows, the thermal decomposition of ozone takes place rapidly. Bloch's report of its production is not accompanied by sufficient experimental detail to enable his conditions to be reproduced. Those chosen in testing for ozone were, therefore, (*a*) the oxidation of sulphur in a U-tube, as already described, and (*b*) the conditions described by Heumann (*loc. cit.*), sulphur being heated in a silica dish supported in a nickel dish (18 cm. diameter). Under these conditions the sulphur vapour oxidises near the heated surface, giving tongues of phosphorescent flame, from which gas may be withdrawn by inserting a funnel attached to a pump. In each instance the oxidation products traversed two narrow, thin-walled U-tubes, cooled to $-124°$ to remove sulphur oxides, and the gas stream then passed over a drop of freshly distilled mercury, the tailing of which was used as a test for ozone.

With method (*a*), the glow being produced at temperatures between 200° and 300° by gas streams containing 8% of oxygen and passing at the rate of 2 l. per hour, no tailing of the mercury drop was observed (10 tests of 1—3 hours' duration each). Using method

(*b*) and the same duration of test, negative results were obtained in each of six tests. Under these conditions, therefore, no ozone is formed in the phosphorescent combustion of sulphur.

Experiments to determine whether a "Glow Pressure" exists in the Oxidation of Sulphur.—Observations on the rate of oxidation of arsenic at different pressures have shown that for each temperature there is a "glow pressure," above which the oxidation is non-luminous, and below which luminescence occurs (Emeléus, J., 1927, 783). A similar examination of the oxidation of sulphur gave negative results. The same method as for arsenic was employed, the apparatus being modified by the addition of a bulb tube immersed in liquid air to a constant depth to freeze out the sulphur dioxide. By this means the rate of oxidation could be followed manometrically. In a series of experiments at 300—340° there was no sudden increase in the oxidation rate as the pressure was reduced, corresponding to the initiation of the glow. Apparently the inhibiting action of sulphur dioxide on the phosphorescent flame is very strong (see below), and the conditions employed did not provide for its sufficiently rapid removal, even at reduced pressures.

The Inhibition of the Phosphorescent Flame of Sulphur.

The large influence of sulphur dioxide in raising the ignition point of sulphur has long been known (compare Moissan, *loc. cit.*). Recently, White (J., 1927, 793) has shown that pentane, acetylene, and methane act similarly. The influence of inhibitors on the phosphorescent stage of the combustion has not, however, been considered, and the experiments described below were directed towards this aspect of the problem. It is suggested that inhibition of the phosphorescence is the primary cause of the raising of the temperature of normal ignition.

Inhibition by Sulphur Dioxide.—In studying the influence of inhibiting substances on the phosphorescent flame, the latter was produced by heating sulphur in a U-tube in a stream of an oxygen–nitrogen mixture, as already described. The depth to which the U-tube was immersed in the furnace was made as small as possible to minimise the formation of sulphur dioxide in the non-luminous oxidation occurring in the tube above the luminous zone. With an 8% oxygen–nitrogen mixture, the influence of varied additions of sulphur dioxide on the temperature of extinction of the glow was first examined, the sulphur dioxide being introduced into the gas stream from a side tube, and the gas composition determined by counting the bubbles in previously calibrated bubblers. The glow was first obtained at a temperature at which the sulphur dioxide

concentration being examined was too small to inhibit it, and the temperature of the furnace was then allowed to fall slowly. The point could thus be found at which the glow disappeared, the observation being made in a dark room with well-rested eyes. The following readings were obtained with a gas stream of 30 c.c. per min. :

Conc. of SO_2 (% by vol. of total gas stream)	0	9·2	19	30	36	44
Temp. of extinction of glow	195°	235°	267°	295°	309°	328°

If, when the glow had disappeared, the temperature was again raised, the luminosity was first observed at a temperature 5—10° higher.

Influence of Organic Vapours.—The action of the vapours of a number of organic liquids was examined by heating the sulphur in a U-tube in a stream of an oxygen–nitrogen mixture (8% oxygen), observing the glow, and then diverting the gas stream through a bubbler containing the liquid in question. It could thus be seen whether the glow diminished in intensity or was extinguished. When inhibition took place the glow invariably reappeared on restoration of the normal gas stream, and could be put out at will, showing that no permanent change in the sulphur surface had taken place. The vapours of the substances tabulated below all inhibited the glow completely over the temperature range stated (temperature of bubblers, 14°). The effect of further increasing the temperature could not be studied, because charring took place, and also because much sulphur dioxide would have been formed in the non-luminous oxidation.

Benzene	270—350°	Ethyl alcohol	300—325°
Toluene	280—325	Ethyl acetate	290—320
Chlorobenzene	270—290	Amyl acetate	295
Pyridine	310	Chloroform	280—300
Ethylene dibromide	280—320	Acetone	220—300

The influence of the concentration of the organic vapour on its effectiveness was not investigated in detail, but the general nature of the result was shown in the case of methyl salicylate, which has a low vapour pressure at room temperature and accordingly has only a weak action on the glow. It was possible to find the temperature at which the luminosity was just inhibited at different concentrations by maintaining the bubbler containing the inhibiting substance at a series of temperatures. The method of observation was the same as that used in the experiments with sulphur dioxide. When the bubbler was maintained at 12°, 24°, and 38°, the glow was extinguished at 243°, 258°, and 268° respectively. Increase in

the concentration of the inhibitor, therefore, raises the temperature at which the glow occurs, as in the oxidation of phosphorus.

Tests were made when the luminous oxidation was inhibited by benzene to determine if any non-luminous oxidation was occurring. A small amount of sulphur dioxide could always be detected by the decoloration of potassium dichromate solution.

Discussion.

As far as can be judged from the nature of the reaction products, the chemical change in the phosphorescent combustion of sulphur is the same as in the normal flame. It is a significant fact that no evidence whatever of the formation of sulphur monoxide was obtained, though the conditions were such that, by analogy with, say, the glow of phosphorus, lower oxidation products would have been produced if they existed. The negative results of the ozone tests show that in this respect, too, the chemiluminescent oxidations of sulphur and phosphorus differ.

Consideration of these inhibition phenomena emphasises the two distinct stages in the oxidation of sulphur, *viz.*, the luminous and the non-luminous oxidation. The dynamics of the latter were investigated by Bodenstein and Caro (*Z. physikal. Chem.*, 1911, **75**, 30), who showed that the reaction rate was proportional to the sulphur surface, and hence, presumably, that the reaction was taking place at this surface. It was also found to be uninfluenced by sulphur dioxide. The slow luminous oxidation is, on the contrary, on the basis of visual observation, a gas reaction, and has been shown to be sensitive to the presence, not only of sulphur dioxide, but also of many other substances. In this, the analogy with the oxidation of phosphorus appears to be very close, and hypotheses as to the mechanism of inhibition of the latter phenomenon have been put forward which may be applied here (*e.g.*, Bäckström, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1927, **6**, No. 16). All contain in essence the idea that " active " molecules are produced in limited numbers, and are essential for the maintenance of the luminous oxidation. The molecules of the inhibiting substances are supposed to be able to deactivate such molecules, and so to hinder the reaction. In the case of the oxidation of sulphur this explanation cannot yet be put in more precise terms.

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CCLV.—*The Constitution of Magnesium Acetate Solutions. Part II. Evidence from Vapour Pressures.*

By E. A. GOODE, NOEL STANLEY BAYLISS, and ALBERT CHERBURY DAVID RIVETT.

IN order to explain qualitatively the relations between concentrations and viscosities, freezing points, and conductivities of solutions of magnesium acetate in water, it has been suggested (J., 1926, 1063) that at high concentrations there is considerable polymerisation of the salt molecules. This association may reasonably be attributed to chelate ring formation where the magnesium atom exercises a co-ordination number of four, and chains (straight or branched) of indefinite extent are built of the unit $>Mg<\begin{matrix}O=C(CH_3)-O \\ O-C(CH_3)=O\end{matrix}>$.

Evidence bearing on this point has now been obtained from a consideration of the lowering of the vapour pressure of water brought about by solution of the salt. For this purpose it was necessary to work at a fairly low temperature (25° was chosen), though this greatly increased the difficulty of accurate measurement. At higher temperatures the tendency to association is decreased, and magnesium acetate falls more nearly into line with most other salts.

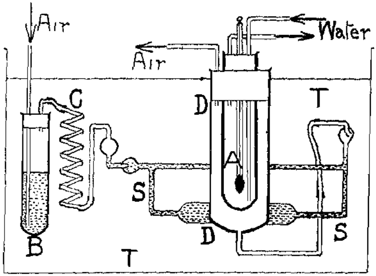
EXPERIMENTAL.

The dew-point method of Cumming (J., 1909, **95**, 1772), as modified by McBain and Salmon (*Proc. Roy. Soc.*, 1920, *A*, **97**, 44), was adopted, its obvious advantages being the rapidity with which measurements can be made and the unimportance of dissolved or entangled air in the solution. With the more viscous solutions, other methods would have been as inapplicable as McBain found them to be for soap solutions. The silver tube A (Fig. 1), on which the dew deposited, was highly polished, the final polishing being done with chamois leather and levigated rouge. McBain's device of dipping part of the tube in boiling water was used. The dew then deposits only on the part which has not been dipped and can be

sharply detected at the boundary. It would seem that dipping removes nuclei, such as traces of dust or polishing material, which are necessary if condensation is to occur. On a very highly polished, undipped tube, it is often difficult to obtain condensation at all, but if the tube be held for an instant in hydrogen chloride fumes, the necessary nuclei are produced at once. Water was circulated through the silver tube from a reservoir heated or cooled as required. Temperatures in the tube and in the surrounding bath (T, Fig. 1) were read to 0·01°.

McBain's procedure, which is suitable for solutions at or near the boiling point and having a vapour pressure of the order of 600 mm., was not satisfactory with such low vapour pressures as those examined at 25°, the complete range of which was from 19 to 25 mm.

FIG. 1.



Thus there was an uncertainty of several tenths of a degree in the dew point as determined for pure water and for some test solutions of potassium chloride: nor was the accuracy improved by exhausting the apparatus. Probably with so little vapour round the tube the rate of diffusion was insufficient. If, however, a current of saturated air was circulated through the system, the accuracy was greatly increased, and differences in successive determinations of dew point were reduced to a few hundredths of a degree. The mean of five measurements of each solution was taken.

Fig. 1 indicates the arrangement adopted. Three saturators, of the type S, contained the solution on which the determination was required. They were separated from one another by a bubbler, B, and a metal coil, C, all immersed in the thermostat, T, and connected as shown with the deposition vessel, D, into which dips the silver tube, A, with its circulating system. It was found inadvisable

to place any solution in D, as the slight splashing on to A tended to obscure the observation.

With a current of laboratory air it was impossible to get satisfactory evidence of condensation. This was no doubt due to the fact that it carried with it impurities like sulphuretted hydrogen which acted upon the dipped silver surface and formed condensation nuclei, thus destroying the contrast between dipped and undipped areas. The trouble was eliminated by passing the air first through a sulphuric acid bubbler and then through a soda-lime tower. We acknowledge our indebtedness to Professor E. J. Hartung for much help in making this apparatus effective.

The success of the method depends upon attainment of complete saturation of the air stream with respect to the solution. Great care must be taken to prevent ingress to the apparatus of traces of water or water vapour.

In making observations, the temperature of appearance of the vapour could be determined much more accurately than that of disappearance. Test measurements with pure water and potassium chloride solutions showed that if the temperature of appearance was taken as the dew point, the error in the vapour-pressure determination was of the order of 0·03 mm. : hence this, and not the mean of the temperatures of appearance and disappearance, was recorded throughout.

Concentrations of solutions were determined after dew-point measurements by evaporating with sulphuric acid a known weight of solution from the last saturator, and weighing the anhydrous magnesium sulphate obtained. They are expressed as g.-mols. per 1000 g. of water (M_w).

Table I gives the results. In the first column is M_w; in the second the temperature of the bath and solution (T_B); and in the fourth that of the dew point (T_D); whilst in the third and fifth are the vapour pressures of pure water (P_B and P_D) at these temperatures, taken from the tables of the International Bureau of Weights and Measures.

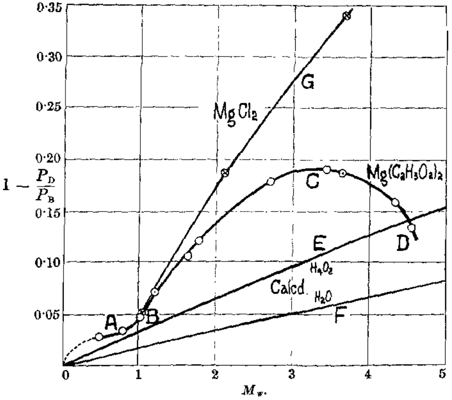
TABLE I.

M_w.	T_B.	P_B.	T_D.	P_D.	$1 - P_D/P_B$.
0·4185	25·03°	23·57	24·55°	22·90	0·028
0·800	25·00	23·52	24·42	22·73	0·034
1·026	24·98	23·50	24·18	22·40	0·047
1·205	25·00	23·52	23·78	21·86	0·071
1·650	24·99	23·51	23·13	21·03	0·106
1·784	25·01	23·54	22·88	20·71	0·120
2·703	25·01	23·54	21·73	19·33	0·179
3·430	25·05	23·60	21·51	19·05	0·192
3·645	25·00	23·52	21·58	19·11	0·187
4·331	25·01	23·54	22·16	19·83	0·158
4·55	24·99	23·51	22·60	20·36	0·134

Discussion of Results.

In discussing results such as these, it is not justifiable to use the vapour-pressure lowerings as a basis for calculating molecular weights of the solute, since, apart from all question of applicability of the gas laws, to do so ignores the fact that the second component, water, is by no means a simple substance, and its behaviour, no less than that of the solute, will affect the vapour pressures. It is best to look at the figures from the point of view of Raoult's law. If this holds, $1 - P_D/P_B$ gives the mean molar fraction of the solute at each concentration. The values obtained experimentally are

FIG. 2.



quoted in the sixth column of the table and they are plotted against M_w in curve ABCD of Fig. 2. For comparison, curves E and F give the molar fractions calculated on the assumptions that the solute particles are simply $Mg(C_2H_3O_2)_2$ and the solvent H_4O_2 (E) or H_2O (F). Lastly, the curve G shows $1 - P_D/P_B$ for magnesium chloride calculated from values obtained by extrapolation to 25° of Tammann's figures for vapour-pressure lowerings (Landolt-Börnstein Tabellen, 5th edition, p. 1386). The contrast with the acetate is very marked, just as it has been found to be in other physical properties.

The "molar fraction" $1 - P_D/P_B$ represents the ratio between

the number of entities of magnesium acetate or its derived products (hydrates, polymerides, or ions) in a given solution and the sum of this number plus that of the free solvent entities. What the latter are, we do not know, but to assume that the molecule is H_4O_2 is probably less incorrect than to take it as H_2O. In any case the qualitative argument is not greatly affected. In dilute solution (A, Fig. 2) the relatively high value of the molar fraction given by the vapour-pressure measurements is undoubtedly due mainly to ionisation of the salt and consequent increase of the numerator in relation to its value calculated on an assumption of the presence of molecules only. The degree of ionic dissociation decreases as concentration increases, so the gradient is not maintained; but after about $M_w = 1$ (B) there is a steady rise which one may assume to be due to a continuous decrease in the denominator of the molar fraction consequent upon the removal of solvent molecules to form hydrates. No doubt such hydration occurs from the beginning, but in dilute solutions the effect on the denominator will be relatively small. In any case it will be in the same direction as the ionisation effect. Presumably the water (whether as single or double molecules or as chains) attaches itself to the Mg radical through the oxygen atom (acting as donor of electrons) to the extent required by the co-ordination number of the ion, which may or may not be also attached to acetate radicals. With magnesium chloride, this continues steadily to high concentrations, but with the acetate a counter-influence of some kind overcomes this hydration effect at C (M_w about 3·25), the curve passing through a maximum. After this point it falls off rapidly, and at D ($M_w = 4{\cdot}5$) it has even come below the molar fraction calculated on an assumption of the presence of undissociated molecules of anhydrous salt and H_4O_2 only. Evidently some cause has reduced the numerator, or increased the denominator, of the molar fraction, or both.

A simple explanation is that at these higher concentrations of magnesium acetate, polymerisation begins to dominate the situation; added molecules link up with others to form complexes of the indeterminate type $>\mathrm{Mg}\genfrac{}{}{0pt}{}{\lessdot A \gtrdot}{\lessdot A \gtrdot}\mathrm{Mg}\genfrac{}{}{0pt}{}{\lessdot A \gtrdot}{\lessdot A \gtrdot}\mathrm{Mg}\genfrac{}{}{0pt}{}{\lessdot A \gtrdot}{\lessdot A \gtrdot}$, in which the magnesium co-ordination number of four is satisfied by two ordinary attachments to hydroxylic oxygen (the respective atoms contributing an electron apiece) and two to the doubly bound oxygen atoms of other acetate radicals (oxygen here contributing both electrons to the covalent bond). When this occurs, any water previously bound will be set free, and so we should get diminution of the numerator as the result of polymerisation, and increase of the denominator as the result of this freeing of previously bound water. Magnesium

chloride cannot form similar rings and chains, so that with it the hydration effect continues unchecked as concentration increases.

The vapour-pressure evidence for magnesium acetate thus supports the view deduced from viscosity and other properties (*loc. cit.*). Lithium acetate, but not potassium, is similar to magnesium acetate, as will be shown later. The property of polymerisation in the way suggested would be expected to appear in the initial rather than the later members of periodic groups.

UNIVERSITY OF MELBOURNE. [*Received, June 6th,* 1928.]

CCLVI.—*The Addition of Halogens to Unsaturated Acids and Esters. Part I. The Addition of Equimolecular Mixtures of Bromine and Chlorine to Cinnamic Acid and its Derivatives in Non-hydroxylic Solvents.*

By NORMAN WILLIAM HANSON and THOMAS CAMPBELL JAMES.

THERE is no direct physicochemical evidence for the existence of a chloride of bromine BrCl, either in the liquid or the solid state (compare Karsten, *Z. anorg. Chem.*, 1907, **53**, 365; Lebeau, *Compt. rend.*, 1906, **163**, 589), but many cases are on record showing that a mixture of bromine and chlorine, dissolved in a suitable solvent, behaves towards ethylenic compounds as though at least some bromine chloride, capable of reacting as a molecule of such, were present. For instance, the addition of the mixed halogens in hydrochloric acid solution to several ethylenic hydrocarbons has been accomplished, the addition products being termed "chlorobromides" (Simpson, *Bull. Soc. chim.*, 1879, **31**, 409; *J. W. James*, J., 1883, **43**, 37; Delépine and Ville, *Compt. rend.*, 1920, **170**, 1390). Further, the last-named authors obtained indications that an equimolecular mixture of dry bromine and chlorine at 0° is much more reactive towards ethylene than either of its constituents separately. By employing a chloroform solution of the mixed halogens, Walden (*Ber.*, 1897, **30**, 2883) achieved their simultaneous addition to maleic anhydride, the product being chlorobromosuccinic anhydride.

By allowing a solution of the mixed halogens in hydrochloric acid to react with cinnamic acid, Erlenmeyer (*Annalen*, 1896, **289**, 259) obtained, along with ω-bromostyrene and phenyl bromohydracrylic acid, about a 50% yield of an acid which he proved to be β-chloro-α-bromo-β-phenylpropionic acid. This was only one of four possible

addition products, *viz.*, the two pairs of externally compensated stereoisomerides corresponding to the formulæ

C_6H_5·CHCl·CHBr·CO_2H (I) and C_6H_5·CHBr·CHCl·CO_2H (II).

The structural isomerides having these formulæ and melting at 182° (I) and 184·5° (II), respectively, have already been described (Glaser, *Annalen*, 1868, **147**, 78; Erlenmeyer, *ibid.*, 1896, **289**, 259).

In the present paper, the addition of equimolecular mixtures of bromine and chlorine, dissolved in carbon tetrachloride or chloroform, to cinnamic acid and some of its derivatives is described. The products of the addition to cinnamic acid have been found to be two acids, both possessing the structure C_6H_5·CHCl·CHBr·CO_2H, melting at 182° and 75°, analogous to the cinnamic acid dihalides (higher-melting) and *allo*-dihalides (lower-melting), respectively, and therefore stereoisomeric. The structure of these acids has been established by an examination of their behaviour when treated with two equivalents of methyl-alcoholic potash. This treatment caused elimination of a mixture of hydrogen chloride and bromide from both acids—no detectable substitution of methoxyl for halogen occurring—and the consequent production of the corresponding monohalogenocinnamic acids. The acid melting at 182° evolved 39% by weight of the available hydrogen bromide, and 61% by weight of the available hydrogen chloride, the products of this elimination being a mixture of acids from which α-bromo-, α-bromo*allo*-, and β-chloro*allo*-cinnamic acids were isolated and identified. The isomeric acid melting at 75° evolved 15% of hydrogen bromide and 84% of hydrogen chloride, the only product isolated being α-bromocinnamic acid. These results demonstrate that the acids are stereoisomerides having the structure C_6H_5·CHCl·CHBr·CO_2H. Further evidence in favour of such a structure is afforded by the fact that a specially prepared specimen of α-chloro-β-bromo-β-phenylpropionic acid proved to be isomeric and not identical with the higher-melting (182°) of these acids, in that it evolved hydrogen bromide only, to the extent of 95% by weight of the available hydrogen bromide, when similarly treated.

These results are in conformity with those obtained from the cinnamic acid dihalides. It is well known that α-hydrogen and β-halogen split off from these acids in preference to the alternative, and also that hydrogen bromide is evolved from the dibromide more readily than hydrogen chloride from the dichloride. The ultimate result in the case of the various chlorobromo-β-phenylpropionic acids would be due to a combination of these two factors. The nature of the products of elimination harmonises with the conclusion that the configurations of the higher- and lower-melting addition products of " bromine chloride " to cinnamic acid are analogous to

those of the cinnamic acid dihalides (higher-melting) and *allo*-dihalides (lower-melting), respectively.

Regarding the relative positions in the molecule taken up by the component atoms of " bromine chloride " when this combines with cinnamic acid, the general rule relating to the addition of diatomic molecules is obeyed, the more negative (*i.e.*, the chlorine) atom attaching itself to the β-carbon atom.

That the rate of addition of " bromine chloride " to cinnamic acid is considerably more rapid than is the case with either of the pure halogens has been shown by a series of kinetic experiments similar in method to those described by Williams and James (this vol., 344). In this case the reaction is bimolecular in type and there is no inhibition period. Corresponding experiments have been carried out with certain substituted cinnamic acids and esters, and in every case examined " bromine chloride " has proved much more reactive than bromine alone, the reaction generally being of the bimolecular type.

Modern theory regarding the interpretation of addition reactions (see Lowry, J., 1923, **123**, 832; Norrish, *ibid.*, p. 2008) postulates a process of unsymmetrical activation, of both the unsaturated molecule and the addendum, which precedes or accompanies such reactions. The cinnamic acid and bromine molecules in this activated state may be represented thus : $C_6H_5\cdot\overset{+}{C}H{=}\overset{-}{C}H\cdot CO_2H$ and $\overset{+}{Br}{-}\overset{-}{Br}$, the bromine molecule breaking up, not into two neutral atoms, but into two ions. Since the rate of addition of bromine to cinnamic acid and its derivatives is generally slow, the ionisation in solution of the former probably occurs to a limited extent.

Experimental evidence points to the conclusion that if a compound of bromine and chlorine—" bromine chloride "—does exist, it must undergo dissociation in solution to such an extent that it escapes physicochemical methods of detection. If—and there is no evidence to the contrary—this dissociation is ionic in nature, then the molecules in solution undergo almost complete disruption into the ions Br^+ and Cl^-, which, being in the activated state, combine rapidly with cinnamic acid. The final interaction between these ions and the activated cinnamic acid molecule would amount merely to a neutralisation of oppositely charged ions, the chlorine ion becoming neutralised by, and uniting with, the β-carbon atom; a similar reaction occurring between the bromine ion and the α-carbon atom.

EXPERIMENTAL.

A finely divided suspension of cinnamic acid in carbon tetrachloride was mixed with one molecular proportion of a solution in

the same solvent of an equimolecular mixture of bromine and chlorine. Complete addition had occurred after exposure to dull light for 4 days. The white powdery product, after filtration and crystallisation from chloroform–carbon tetrachloride, melted at 182° as described by Erlenmeyer (*loc. cit.*) (Found: Br, 30·9; Cl 13·5. Calc. for $C_9H_8O_2ClBr$: Br, 30·3; Cl, 13·5%).

The filtrate after removal of this product yielded on evaporation a thick, colourless oil which solidified in a vacuum. After crystallisation from light petroleum the substance consisted of small colourless prisms, m. p. 75°. Analysis and the reactions described below indicate that it is stereoisomeric with the substance melting at 182° and is therefore the lower-melting (*allo*-) β-*chloro*-α-*bromo*-β-*phenylpropionic acid*, C_6H_5·CHCl·CHBr·CO_2H (Found: Br, 30·9; Cl, 13·2. $C_9H_8O_2ClBr$ requires Br, 30·3; Cl, 13·5%).

In a series of experiments carried out under the conditions described, the proportion of the higher- to the lower-melting product was approximately 1 : 3.

The isomeric α-chloro-β-bromo-β-phenylpropionic acid was prepared by converting cinnamic acid into its chlorohydrin (compare Read and Andrews, J., 1921, **119**, 1774), and replacing the hydroxyl group by bromine by means of concentrated hydrobromic acid (Glaser, *Annalen*, 1868, **147**, 78). The distinction between this acid, m. p. 184·5°, and the acid described above, m. p. 182°, has been established by Erlenmeyer (*loc. cit.*).

The action of methyl-alcoholic potash on these three acids has been investigated, under conditions which would extract one equivalent only of hydrogen halide. About 0·5 g. of each acid was warmed with exactly 2 equivalents of alkali on a water-bath, the alcohol being subsequently evaporated. The residues were dissolved in water and acidified with dilute nitric acid, the precipitated organic acids were filtered off and washed, and the filtrate was analysed for chloride and bromide. The results indicated that the following proportions of hydrogen chloride and hydrogen bromide were extracted:

Acid, m. p.	% HCl *extracted.*	% HBr *extracted.*
182°	61	39
75	84	15
184·5	0	95

The products of these reactions were isolated in experiments conducted on a larger scale.

Acid, m. p. 182°. The acid (7 g.) was dissolved in methyl alcohol and treated with methyl-alcoholic potash (2 equivs.). The solvent was evaporated, the residue taken up with water, and a slight excess of 10% barium chloride solution added (compare Sudborough and

Thompson, J., 1903, **83**, 673; Sudborough and James, J., 1906, **89**, 107). After 3 hours, the sparingly soluble barium salt was removed and this and the filtrate were treated separately with dilute acid. The sparingly soluble salt yielded 1·3 g. of acid which on recrystallisation from benzene had melting point 131° and proved to be α-bromocinnamic acid. The filtrate gave 3·5 g. of acid of low melting point from which by fractional crystallisation from chloroform and light petroleum were isolated (1) α-bromo*allo*cinnamic acid, m. p. 120°, and (2) β-chloro*allo*cinnamic acid, m. p. 131—132°.

Acid, m. p. 75°. 5 G. were treated as above and yielded 3·5 g. of α-bromocinnamic acid (m. p. 131°) as the only recognisable product.

The results of kinetic experiments are summarised in the tables. Table I gives the values for the bimolecular velocity coefficient $k=1/t \, . \, x/a(a-x)$, based upon time (t) in hours and concentrations (a and x) in g.-mols. per litre for "bromine chloride," and for comparison Table II gives results for bromine alone under similar conditions.

The substances examined were (1) † cinnamic acid, (2) † α-methylcinnamic acid, (3) † methyl *o*-methoxycinnamate, (4) † methyl *o*-methoxy*iso*cinnamate, (5) * α-bromo-*o*-methoxycinnamic acid, (6) * *m*-methoxycinnamic acid, and (7) † methyl *m*-methoxycinnamate.

TABLE I. TABLE II.

Temperature 0°.

Substance.	Table I. Limits of k.	Table I. Mean k.	Table II. Limits of k.	Table II. Mean k.
1	113—96·3	104	0·173—0·041	0·146
2	2·83—2·07	2·51	0·013—0·011	0·012
3	2730—2032	2382	13·3 (0·117)—5·47 (9·27)	—
4	5682—4412	5009	44·9 (0·200)—18·9 (8·29)	—
5	124 (0·038)—59·2 (2·51)	—	0·158—0·123	0·137
6	4166 (0·018)—922 (0·292)	—	79·2 (0·030)—3·97 (61·5)	—
7	243—182	199	1·24—0·717	1·09

The figures in parenthesis denote the time (in hours) at which the value of k is that which precedes them. In such cases the reaction is not bimolecular and k varies with t.

The value of the velocity coefficient for the addition of chlorine to cinnamic acid under similar conditions was found to be 0·209.

Summary.

An equimolecular mixture of bromine and chlorine, dissolved in carbon tetrachloride, has been found to react additively with cinnamic acid as bromine chloride, were such a compound existent, the

* Indicates reactions in chloroform as solvent.

† Indicates reactions in carbon tetrachloride as solvent.

product of addition being the two stereoisomeric β-chloro-α-bromo-β-phenylpropionic acids.

Such a "bromine chloride" solution has been shown kinetically to react at a far more rapid rate with cinnamic acid and some of its derivatives than bromine solution itself. These phenomena appear to be readily explicable along the lines of modern polarity theories.

One of us (N. W. H.) desires to express his indebtedness to the Department of Scientific and Industrial Research for a maintenance grant.

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ABERYSTWYTH. [*Received, May 11th, 1928.*]

CCLVII.—*Steric Hindrance in Reactions of Substituted Quinoxalines.*

By GEORGE MACDONALD BENNETT and GERVASE HEWITSON WILLIS.

IT has long been known that a methyl group occupying the α- or the γ-position to the nitrogen atom of a pyridine or quinoline nucleus possesses a high reactivity towards aldehydes and other reagents, which in the β-position it does not possess. The methyl groups of 2 : 3-dimethylquinoxaline, $C_6H_4<\begin{matrix}N:CMe\\N:CMe\end{matrix}$, are each in the α-position with respect to one nitrogen atom of the heterocyclic nucleus, but each is at the same time in the β-position with respect to the second nitrogen atom. It therefore seemed possible that these methyl groups would be of the non-reactive or at least of a less reactive type. The observation that in this dimethylquinoxaline both methyl groups have a high reactivity of the kind specified was of sufficient interest to warrant a detailed study.

We have examined the behaviour of 2-methyl-, 2 : 3-dimethyl-, and 2 : 3 : 6-trimethyl-quinoxalines, 2-phenyl-3-methylquinoxaline, 2-benzylquinoxaline, and 2-*p*-methoxy- and 2-*p*-chloro-benzyl-3-phenylquinoxaline with a number of aldehydes and with bromine. The 2 : 3-dimethyl base has also been condensed with ethyl oxalate.

Although a quantitative comparison was not practicable, it is clear that 2 : 3-dimethylquinoxaline reacts with aromatic aldehydes with approximately the same ease as does quinaldine. The reactivity is no doubt due to the simultaneous effects of general and alternating polar influences. Polarisations leading to reaction are possible if a methyl group is placed α- to a nuclear nitrogen atom and the second nitrogen atom does not interfere with this. Its general polar

effect will in fact tend to increase the reactivity of the molecule. The experiments of Mills and others (J., 1922, **121**, 2724; 1925, **127**, 2466) indicate that the polarisation in question here may proceed as far as complete tautomeric change into a more reactive isomeride. From this point of view it is not surprising that Lapworth and Higginbotham (J., 1922, **121**, 2823) found no reactivity in the methyl groups of *m*-methoxytoluene and 3 : 5-dimethoxytoluene and that we similarly failed to induce reaction between an aromatic aldehyde and *m*-dimethylaminotoluene. A possible reactive tautomeric form cannot in these cases be formulated.

It should, however, be pointed out that even if this reactivity of the methyl group arises only where tautomeric change is possible it does not follow that completed isomeric change precedes reaction. The activated molecule which reacts may, in fact, occupy an intermediate position between the methylene base $-NH\cdot\overset{|}{C}{:}CH_2$ and the methyl base $-N{:}\overset{|}{C}\cdot CH_3$. In the closely analogous case of keto-enolic tautomerism, where the enolic forms are known to be more reactive with bromine than the keto-forms, the experiments of Leuchs (*Ber.*, 1913, **46**, 2435: compare Robinson, J., 1917, **111**, 963) indicate that complete enolisation does not precede the reaction.

The products of condensation of 2 : 3-dimethylquinoxaline with aromatic aldehydes are distyrylquinoxalines (I), but in the reactions with certain aldehydes such as *o*- and *p*-methoxybenzaldehydes and *m*-nitrobenzaldehyde a monostyryl derivative was isolated in place of, or in addition to, the other. The formula (II) was a conceivable alternative to (III) for these substances, but the latter is undoubtedly correct, since the products decolorise cold solutions of bromine and permanganate. Moreover, the substance from *m*-nitrobenzaldehyde was shown to react further with the nitro-aldehyde with production of the distyrylquinoxaline of type (I), a reaction which points conclusively to the formula (III).

$$\text{(I.)}\quad C_6H_4{<}\begin{matrix}N{:}C\cdot CH{:}CHAr\\ |\\ N{:}C\cdot CH{:}CHAr\end{matrix}\qquad\qquad C_6H_4{<}\begin{matrix}N{:}C\cdot CH_2\\ |\\ N{:}C\cdot CH_2\end{matrix}{>}CHAr\quad\text{(II.)}$$

$$C_6H_4{<}\begin{matrix}N{:}C\cdot CH_3\\ |\\ N{:}C\cdot CH{:}CHAr\end{matrix}\quad\text{(III.)}$$

Condensation with benzaldehyde and piperonal was best brought about by heating the mixture to the boiling point in the absence of catalysts, but in all other cases the reactants were heated together in boiling acetic anhydride for a few hours. A comparison of the behaviour of some fifteen aromatic aldehydes with the 2 : 3-dimethyl base shows that those containing the nitro-group are distinguished by their rapid condensation, yielding styryl derivatives which are

easily isolated, as they crystallise directly from the reaction mixture. 2 : 3-Dimethylquinoxaline furnishes upwards of 50% of the calculated yield of product when condensed in acetic anhydride with *o*-, *m*-, or *p*-nitrobenzaldehyde, 2 : 4-dinitrobenzaldehyde, or *o*- or *p*-chlorobenzaldehyde. In particular, *p*-nitro- and 2 : 4-dinitrobenzaldehydes are convenient reagents for detecting the reactive methyl group of a base. There is little doubt that these aldehydes will react equally readily with other heterocyclic bases, and we have confirmed this in the case of three substituted quinolines.

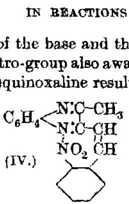
On the other hand, the products from the three methoxybenzaldehydes were obtained in lower yield. Although this may have been partly due to the greater difficulty of their isolation, there can be no doubt that the methoxy-aldehydes react more slowly. Moreover *o*-methoxybenzaldehyde yielded solely the monostyryl *derivative (III; Ar = C_6H_4·OMe). This compound decolorises cold* solutions of permanganate and bromine and yet was recovered unchanged after a second heating with *o*-methoxybenzaldehyde.

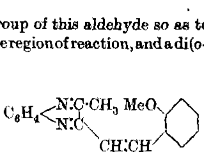
It is thus clear that the reaction of 2 : 3-dimethylquinoxaline proceeds easily with most substituted benzaldehydes, including those with a nitro-group or a chlorine atom in the *o*-position, yet the second stage of the reaction is inhibited when an *o*-methoxy-group is present. If this effect were solely due to steric hindrance, the nitro-group would be expected to have at least as great an influence as the methoxy-group. We suggest that the explanation is to be found in the polar characters of the various atoms and groups and in the forces of attraction and repulsion which arise between them. It is known that nitro-compounds are able to unite with bases, union presumably taking place between the nitro-group and the nitrogen atom of the base, and an attraction must therefore exist between a nitro-group of the mono- or di-nitrobenzaldehyde and the nitrogen atom of the quinoxaline. Direct confirmation of this was obtained by the isolation of a "molecular" *compound*,

$$C_{10}H_{10}N_2,2C_6H_3(NO_2)_2\cdot CHO,$$

from the two reactants in a case where high reactivity had been found. This is of interest as affording evidence of direct union of the reacting molecules as a prelude to the condensation. Moreover it appears probable that this attraction of the nitro-group to the tertiary nitrogen atom will continue to operate within the molecule of the nitrostyryl derivative first formed. Consequently the latter substance will for a large proportion of the time assume a configuration such as (IV), in which the large nitrostyryl residue is held remote from the second methyl group in the quinoxaline nucleus. Reaction of (IV) with a second molecule of *o*-nitrobenzaldehyde will be unhindered, a similar force operating between the second nitrogen

atom of the base and the nitro-group of this aldehyde so as to keep this nitro-group also away from the region of reaction, and a di(o-nitrostyryl)quinoxaline results.


(IV.)


(V.)

The force which is involved in the condensation with *o*-methoxybenzaldehyde, on the other hand, should be one of repulsion between the methoxy-group and the basic nitrogen atoms. The reaction is therefore slower and the monostyrylquinoxaline first produced tends for the greater portion of the time to adopt a spatial arrangement such as (V). Access of a second molecule of the aldehyde to the remaining methyl group of the base will now be very difficult. If further reaction were to take place, the adjacent nitrogen atom would tend to force the methoxy-group of this aldehyde molecule into the space around the methyl group already crowded in (V). The second stage of the reaction is thus completely arrested by a steric hindrance depending for its operation on the polar nature of the groups involved.

In order to test this conception we examined the reaction of the quinoxaline with *o*-iodobenzaldehyde. The iodine atom is known to have a large steric effect in such reactions as the esterification of acids, but it has the same type of general polar effect as the nitro-group and might be expected to have a similar attraction for a basic nitrogen atom. Experiment confirmed the expectation that steric hindrance would therefore be absent, for a good yield of di(*o*-iodostyryl)quinoxaline was isolated.

The effect here discussed is seen to be a true steric hindrance, although its operation may depend on the control of configuration by polar forces. The apparent steric hindrance of a reaction may arise from at least three distinct causes, namely (*a*) true steric hindrance, (*b*) the influence (other than steric) of the hindering group on the reactivity of the active group, (*c*) direct chemical action between the groups of the kind suggested by Sidgwick and Callow (J., 1924, **125**, 527). The distinction between these may be uncertain in some cases, and a polar force may, as above suggested, be involved in evoking effects of type (*a*). A similar explanation may be offered of the observation of Remsen and Reid (*Amer. Chem. J.*, 1899, **21**, 340) that *o*-methoxybenzamide is hydrolysed faster than *o*-chlorobenzamide, a true steric hindranee (*a*) being controlled by a repulsion and an attraction respectively between the groups involved.

The variations in reactivity recorded by Dyson, George, and Hunter (J., 1927, 436), however, are apparently due to effects of type (*b*) and not to steric hindrance.

A less extended series of experiments with 2 : 3 : 6-trimethylquinoxaline served on the whole to confirm the conclusions arrived at with the dimethyl base. The third methyl group is not in a position to be reactive, but it shows its presence by a distinct increase of reactivity in the other two methyl groups. The 6-methyl group no doubt exerts an effect on the nitrogen atoms similar to that which causes *m*- and *p*-toluidines to be stronger bases than aniline. The nitrogen atoms of the quinoxaline consequently cause a somewhat greater activation of the 2- and 3-methyl groups.

The base 2-phenyl-3-benzylquinoxaline was included in our study because the methylene group of the benzyl group seemed likely to show an enhanced reactivity due to the attached phenyl nucleus (compare Skraup and Böhm, *Ber.*, 1926, **59**, 1007). Substituted benzyl bases could easily be prepared by the method of Malkin and Robinson (J., 1925, **127**, 369), but we found that neither the benzyl nor the *p*-methoxy- nor *p*-chloro-benzyl bases reacted at all under the conditions of our experiments. The reaction is here inhibited by the combined steric hindrance of the phenyl radicals in position 2 and in the benzyl group of position 3, for we obtained good yields of styryl derivatives from 2-phenyl-3-methylquinoxaline on the one hand and from 2-benzylquinoxaline on the other. That a single *o*-methyl group exerts little or no steric hindrance in this reaction is shown by the easy condensation with 2 : 3-dimethylquinoline.

Through the kindness of Dr. F. M. Hamer, who supplied us with a specimen of the quinoxaline of *cyclo*pentadione, we were able to examine this base also. It reacts readily with aldehydes, although markedly less rapidly than the 2 : 3-dimethyl base, and the products have the structure $C_6H_4<\begin{matrix}N:C\cdot C(:CHAr)\\N:C\cdot C(:CHAr)\end{matrix}>CH_2$.

The *methiodide* of 2 : 3-dimethylquinoxaline was prepared in order to test its capacity to undergo condensations similar to those of quinaldine methiodide. Unexpected difficulty was found in its preparation, only resinous products being at first produced. Subsequently a good yield of a monomethiodide was obtained by heating the base in a large excess of methyl iodide. It is possible that this method would yield quaternary salts in some other cases of recorded difficulty (*e.g.*, the substituted quinazolines; Bogert and Clark, *J. Amer. Chem. Soc.*, 1924, **46**, 1294). The methiodide reacted with aldehydes and with nitrosodimethylaniline, but the products were black, insoluble solids which it was found impossible to purify. Repeated trials showed no reaction between the methiodide and

quinoline methiodide in alkaline solution to yield a dye of the *iso*cyanine type, nor with formaldehyde present to give a carbocyanine.

The bromination of these quinoxalines was studied under the standard conditions of heating the substance at 100° in acetic acid with bromine and sodium acetate. 2-Methylquinoxaline yielded the expected ω-tribromo-compound analogous to that obtained from quinaldine. In other cases, steric hindrance supervened, 2 : 3-dimethylquinoxaline being converted into a tetrabromo-derivative which resisted further bromination. This may be compared with the tetrabromo-compound from *o*-xylene (Gabriel and Müller, *Ber.*, 1895, **28**, 1830). It has the symmetrical structure (VI) and not the alternative (VII), for on hydrolysis with silver acetate it is converted into a substance giving an immediate precipitate with *p*-nitrophenylhydrazine. A similar steric hindrance is apparent in the formation of the dibromo-derivative (VIII) from phenylmethylquinoxaline.

$$C_6H_4\Big\langle\begin{array}{l}N{:}C\cdot CHBr_2\\ N{:}C\cdot CHBr_2\end{array} \qquad C_6H_4\Big\langle\begin{array}{l}N{:}C\cdot CH_2Br\\ N{:}C\cdot CBr_3\end{array} \qquad C_6H_4\Big\langle\begin{array}{l}N{:}C\cdot CHBr_2\\ N{:}CPh\end{array}$$

(VI.) (VII.) (VIII.)

When benzyl- and chlorobenzyl-phenylquinoxalines were subjected to the same reaction, the products isolated were free from bromine, and were identified as the acetoxy-compounds (IX) and (X). These substances must evidently have been produced by the

$$\text{(IX.)}\quad C_6H_4\Big\langle\begin{array}{l}N{:}CPh\\ N{:}C\cdot CHPh\cdot OAc\end{array} \qquad C_6H_4\Big\langle\begin{array}{l}N{:}CPh\\ N{:}C\cdot CH(C_6H_4Cl)\cdot OAc\end{array}\quad\text{(X.)}$$

interaction of a monobromo-compound with the sodium acetate present. The bromo-compound (XI), which must thus be an intermediate product, would have a particularly reactive bromine atom similar to that of diphenylmethyl bromide.

$$\text{(XI.)}\quad C_6H_4\Big\langle\begin{array}{l}N{:}CPh\\ N{:}C\cdot CHPhBr\end{array} \qquad C_6H_4\Big\langle\begin{array}{l}N{:}C\cdot CH_2\cdot CO\cdot CO_2Et\\ N{:}C\cdot CH_3\end{array}\quad\text{(XII.)}$$

2 : 3-Dimethylquinoxaline reacts with ethyl oxalate, in the presence of either sodium or potassium ethoxides (compare the reactions of quinaldine examined by Wislicenus, *Ber.*, 1897, **30**, 1479; 1909, **42**, 1140) to yield *ethyl 2-methylquinoxaline-3-pyruvate* (XII), the structure of which is confirmed by the formation of a *p-nitrophenylhydrazone*.

The 2 : 3-dimethyl base did not react with amyl nitrite, Michler's hydrol, *p*-nitrosodimethylaniline, or a 2 : 4-dinitrobenzenediazonium salt.

EXPERIMENTAL.

Preparation of the Quinoxalines.—The method of Böttcher (*Ber.*, 1913, **46**, 3084) for preparing 2-methylquinoxaline was modified as follows: *iso*Nitrosoacetone (37 g.) and o-phenylenediamine (44 g.) were boiled in a mixture of hydrochloric acid (15 g.; *d* 1·19), glacial acetic acid (25 c.c.), and water (75 c.c.). The resultant mixture was made alkaline and benzoylated by means of benzoyl chloride (50 g.). The product was removed in a current of steam, and the distillate extracted with ether. The extract was dried over anhydrous sodium sulphate, the ether removed, and the residue distilled in a vacuum. The substance had b. p. 118°/16 mm. (yield, 13 g. or 45%).

2 : 3-*Dimethylquinoxaline* was obtained from methyl ethyl ketone through the *iso*nitroso-compound (compare Gabriel and Sonn, *Ber.*, 1907, **40**, 4850), the latter being used in the form of the crude oil which separates on acidification of the alkaline reaction mixture (yield, 70%).

2 : 3 : 6-Trimethylquinoxaline was readily obtained by a similar process.

2-Phenyl-3-methylquinoxaline (Auwers, *Ber.*, 1917, **50**, 1182) was not detected in the products of interaction of *iso*nitrosopropiophenone and *o*-phenylenediamine, but was prepared by heating the diketone (Smedley, J., 1909, **95**, 218) and the diamine together in ethyl alcohol for ½ hour.

Benzylglyoxal was prepared as described by Dakin and Dudley (*J. Biol. Chem.*, 1914, **18**, 42), except that the presence of any large amount of dibenzyl was avoided by preparing the magnesium benzyl chloride as recommended by Gilman and Myers (*J. Amer. Chem. Soc.*, 1923, **45**, 2462). Hydrolysis of the acetal (b. p. 131°/4 mm. 148—151°/18 mm.) from 20 g. of diethoxyacetopiperidide yielded at once the practically pure benzylglyoxal of m. p. 117—118° (3·8 g.)

2-*Benzylquinoxaline* was obtained as a dark oil, which did no solidify, by heating benzylglyoxal and *o*-phenylenediamine (1 mol for 20 minutes in ethyl alcohol. The *picrate* forms yellow needle m. p. 117°, from ethyl alcohol (Found: N, 15·9. $C_{21}H_{15}O_7N$ requires N, 15·6%).

*Phenyl β-methoxy-*p*-chlorostyryl ketone*, Ph·CO·C(OMe):CH·C_6H_4(was obtained from ω-methoxyacetophenone (4·6 g.) by condensati with *p*-chlorobenzaldehyde and was isolated as an oil, b. p. 238°/ mm. (yield, 5·7 g.), which solidified on keeping and was crystallis (m. p. 45°) from light petroleum (Found: Cl, 13·0. $C_{16}H_{13}O_2$ requires Cl, 13·0%).

Phenyl p-*Chlorobenzyl Diketone.*—A solution of the foregoi substance (2 g.) in acetic acid (9 c.c.) and concentrated hydrobron acid (4 c.c.) was heated until the yellow solution acquired a green

hue; it was then cooled and diluted. The product (1·8 g.) was isolated by means of ether and recrystallised from light petroleum; m. p. 85° (Found: Cl, 13·4. $C_{15}H_{11}O_2Cl$ requires Cl, 13·7%). This substance differs from the corresponding methoxybenzyl compound (Malkin and Robinson, *loc. cit.*) in not being appreciably extracted from its ethereal solution by aqueous alkalis.

2-p-*Chlorobenzyl-3-phenylquinoxaline*.—The diketone condensed with *o*-phenylenediamine in alcoholic solution to yield this quinoxaline, but a more convenient mode of procedure was as follows: To the solution obtained by heating phenyl β-methoxy-*p*-chlorostyryl ketone (5 g.) in acetic acid (22 g.) and hydrobromic acid (10 c.c.), as previously described, *o*-phenylenediamine (2 g.) was added, and the mixture boiled with addition of ethyl alcohol until a homogeneous solution resulted. Crystals of the quinoxaline separated as the solution cooled, and after recrystallisation from ethyl alcohol had m. p. 142° (yield, 5·5 g.) (Found: Cl, 10·6. $C_{21}H_{15}N_2Cl$ requires Cl, 10·7%).

Phenyl β : 3-Dimethoxystyryl Ketone.—The product from ω-methoxyacetophenone (27·2 g.) and *m*-methoxybenzaldehyde was an oil of b. p. 245°/18 mm. (27·8 g.) (Found: C, 75·5; H, 6·0. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%). Hydrolysis of this with acetic and hydrobromic acids yielded a pinkish solid which, after being crystallised from light petroleum, melted at 175—180° (decomp.) when rapidly heated. This *substance* was not the expected diketone but apparently a polymeride, which did not react with *o*-phenylenediamine and was not further investigated (Fouud: C, 75·6; H, 5·7; *M*, 474. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%; *M*, 254).

Condensation of 2-Methylquinoxaline with Aldehydes.—In each case a solution of the base (1 mol.) and an aldehyde (1 mol.) in acetic anhydride (5—6 mols.) was boiled for a certain period of time: the product separated in the crystalline condition on cooling.

2 : 4-Dinitrobenzaldehyde gave *2-(2 : 4-dinitrostyryl)quinoxaline* (yield, after 1 hour, 80%), which was recrystallised from hot aqueous acetic acid; m. p. 219—220° (decomp.) (Found: N, 17·6. $C_{16}H_{10}O_4N_4$ requires N, 17·4%).

2-o-*Nitrostyrylquinoxaline*, formed from *o*-nitrobenzaldehyde (yield, after 3 hours, 78%), crystallised from toluene in pale yellow needles, m. p. 156° (Found: N, 15·1. $C_{16}H_{11}O_2N_3$ requires N, 15·2%).

2-m-*Nitrostyrylquinoxaline*, from *m*-nitrobenzaldehyde (yield, after 4 hours, 68%), crystallised from equal volnmes of benzene and petroleum (b. p. 60—80°) in almost colourless needles, m. p. 199·5° (Found: N, 15·3%).

2-p-*Nitrostyrylquinoxaline*, from *p*-nitrobenzaldehyde (yield, after

¾ hour, 65%), crystallised from toluene in pale yellow needles, m. p. 200° (Found: N, 15·3%).

The base appeared to react with benzaldehyde, but the product was not obtained crystalline.

Condensation of 2 : 3-Dimethylquinoxaline with Aldehydes.—2 : 3-Dimethylquinoxaline was boiled in solution in excess of benzaldehyde for 2 hours. On cooling, 2 : 3-*distyrylquinoxaline* was deposited as a yellow solid which crystallised from a mixture of equal proportions of xylene and light petroleum (b. p. 90—120°) in yellow monoclinic needles, m. p. 190·5° (yield, 50—70%) (Found: C, 86·2; H, 5·3; N, 8·5; *M*, 363. $C_{24}H_{18}N_2$ requires C, 86·25; H, 5·4; N, 8·4%; *M*, 334). No monostyrylmethylquinoxaline could be detected whatever the conditions of the reaction. Oxidation of the substance in acetone solution by potassium permanganate yielded no crystalline product other than benzoic acid. The action of bromine in boiling chloroform produced after 3 hours a *tetrabromide*, which was isolated by evaporation of the solvent and obtained in silvery plates, m. p. 190° (depressed to 177° by admixture of distyrylquinoxaline), by crystallisation from benzene (Found: Br, 48·1. $C_{24}H_{18}N_2Br_4$ requires Br, 48·3%).

2 : 3-Dimethylquinoxaline was boiled with piperonal (1 mol.) in acetic anhydride (5—6 mols.) for 5 hours, and the mixture distilled in a current of steam. The residue of 2-*methylenedioxystyryl-3-methylquinoxaline* solidified on keeping (yield, 20%) and after crystallisation from benzene–light petroleum and again from methyl alcohol was obtained in lemon-yellow needles, m. p. 150° (Found: N, 9·5. $C_{18}H_{14}O_2N_2$ requires N, 9·7%). When the heating was prolonged, a trace of a substance of higher melting point was observed among the products. This was prepared in quantity by boiling 2 : 3-dimethylquinoxaline with an excess of piperonal for 4 hours, removing the latter in boiling water, and crystallising the crude solid product from ethyl alcohol. 2 : 3-*Di(methylenedioxystyryl)quinoxaline* was then obtained in yellow monoclinic needles, m. p. 208° (yield, 30%) (Found: C, 73·8; H, 4·4; N, 6·8. $C_{26}H_{18}O_4N_2$ requires C, 73·9; H, 4·3; N, 6·6%). Addition of zinc chloride to the reaction mixture in this preparation did not improve the yield and made the purification less easy.

In the following preparations the base (1 mol.) and the required aldehyde (1 mol.) were heated in boiling acetic anhydride (5—6 mols.) for varying periods. The mixture was distilled in a current of steam, and the residue dried and crystallised.

The product obtained with *m*-nitrobenzaldehyde after 6 hours' heating was fractionally crystallised from benzene. The larger and more insoluble portion was recrystallised from this solvent an

2 : 3-*di*(m-*nitrostyryl*)*quinoxaline* obtained in small yellow bi-pyramids, m. p. 237° (yield, 10%) (Found: C, 67·8; H, 3·8; N, 13·3. $C_{24}H_{16}O_4N_4$ requires C, 67·9; H, 3·8; N, 13·2%). The smaller, more soluble, fraction was 2-m-*nitrostyryl*-3-*methylquinoxaline*, which crystallised from aqueous methyl alcohol in almost colourless needles, m. p. 184° (yield, 1—2%) (Found: C, 70·0; H, 4·4; N, 14·5. $C_{17}H_{13}O_2N_3$ requires C, 70·1; H, 4·5; N, 14·4%). This substance rapidly decolorised solutions of potassium permanganate and of bromine. When it was heated in boiling acetic anhydride with *m*-nitrobenzaldehyde it was converted into the foregoing di(*m*-nitrostyryl)quinoxaline of m. p. 237°.

The oily product from *p*-methoxybenzaldehyde, after 7 hours' heating, solidified on keeping. It was separated into two fractions by means of methyl alcohol. The less soluble portion was 2 : 3-*di*(p-*methoxystyryl*)*quinoxaline*, which crystallised from light petroleum (b. p. 90—120°) in yellow needles, m. p. 163° (yield, 10%) (Found: N, 7·3. $C_{26}H_{22}O_2N_2$ requires N, 7·1%). The more soluble fraction was 2-p-*methoxystyryl*-3-*methylquinoxaline*, which crystallised in rosettes of yellow needles, m. p. 122·5° (yield, 10%) (Found: N, 10·3. $C_{18}H_{16}ON_2$ requires N, 10·1%).

The following preparations were carried out as before, except that two molecular proportions of aldehyde were used.

2 : 3-*Di*(m-*methoxystyryl*)*quinoxaline* was obtained with *m*-methoxybenzaldehyde after 4 hours' heating and crystallised from ethyl alcohol in yellow prisms, m. p. 126° (yield, 10%) (Found: N, 7·3. $C_{26}H_{22}O_2N_2$ requires N, 7·1%).

2-o-*Methoxystyryl*-3-*methylquinoxaline* was isolated with some difficulty from the reaction with *o*-methoxybenzaldehyde after 6½ hours' heating. It was extracted in light petroleum, and crystallised from methyl alcohol in microscopic yellow crystals, m. p. 112° (yield, 1—2%) (Found: N, 10·1. $C_{18}H_{16}ON_2$ requires N, 10·1%). This compound rapidly decolorises solutions of permanganate and of bromine. It was recovered entirely unchanged after being heated in boiling acetic anhydride for 12 hours with *o*-methoxybenzaldehyde (2 mols.).

2 : 3-*Di*(3 : 4-*dimethoxystyryl*)*quinoxaline* was obtained from 3 : 4-dimethoxybenzaldehyde in a similar manner. It crystallised from ethyl alcohol in yellow needles, m. p. 208° (yield, 10%) (Found: N, 6·3. $C_{28}H_{26}O_4N_2$ requires N, 6·2%).

2 : 3-*Di*(β-*furylvinyl*)*quinoxaline* was obtained from furfural after 5 hours' heating, and crystallised from light petroleum (b. p. 90—120°) in yellow crystals, m. p. 169° (yield, 5%) (Found: N, 9·0, $C_{20}H_{14}O_2N_2$ requires N, 8·9%).

In the following preparations with nitro- and halogenated benz-

aldehydes distillation in steam was unnecessary, as the product crystallised when the mixture cooled.

2 : 3-*Di*(o-*nitrostyryl*)*quinoxaline* (yield, after 3 hours, 80%) crystallised from benzene in star-shaped groups of needles, m. p. 194·5° (Found : N, 13·5. $C_{24}H_{16}O_4N_4$ requires N, 13·2%).

2 : 3-*Di*(p-*nitrostyryl*)*quinoxaline* (yield, after 1½ hours, 75% crystallised from nitrobenzene in deep yellow crystals, m.p. 288° (decomp.) (Found : N, 13·3%).

2-(2 : 4-*Dinitrostyryl*)-3-*methylquinoxaline* (yield, after 1 hour, 80%) separated from *cyclo*hexanol in orange-yellow crystals, m. p. 224—225° (decomp.) (Found : C, 60·5 ; H, 3·4 ; N, 16·9. $C_{17}H_{12}O_4N_4$ requires C, 60·7 ; H, 3·6 ; N, 16·7%). This substance rapidly decolorised solutions of permanganate and of bromine. The only product isolated after oxidation with potassium permanganate in acetone solution was 2 : 4-dinitrobenzoic acid (m. p. 177—179°). It was found possible also to produce the above compound by condensation in glacial acetic acid, or in xylene in the presence of a trace of zinc chloride. On the other hand, molecular proportions of the base and dinitrobenzaldehyde in solution in benzene were found to yield, after the expiration of 10 days, a considerable quantity of crystals of m. p. 96—97°. Admixture with a little of the base lowered the m. p. Fractional crystallisation from light petroleum yielded the quinoxaline and the aldehyde. The substance is, in fact, an *addition compound* of the base and the aldehyde, decomposed in hot petroleum. The variation of m. p. with composition of a mixture of the two substances shows the compound to contain 2 molecules of aldehyde to 1 molecule of base :

Dinitrobenzaldehyde (mols. %)	100	97·6	75	66·7	52·4
M. p.	71°	71°	75°	91°	80·5°
Dinitrobenzaldehyde (mols. %)	50	47·6	33·3	25·0	0
M. p.	72°	74°	81°	88°	106°

In view of the direct formation of a di-(2 : 4-dinitrostyryl) derivative from 2 : 3 : 6-trimethylquinoxaline (p. 1972) it seemed likely that an analogous compound would be formed from the 2 : 3-dimethyl base. The isolation of the above monostyryl derivative might be accounted for by its relative insolubility and its consequent removal from the reaction by crystallisation. This was confirmed as follows The 2 : 3-dimethyl base, heated for 8 hours with the dinitro-aldehyde (3 mols.) in an excess of acetic anhydride, furnished 2 : 3-*di*(2 : 4-*dinitrostyryl*)*quinoxaline* (yield, 75%), which crystallised in brown needles from hot nitrobenzene and melted at 295—297° (decomp. (Found : C, 56·1 ; H, 3·0. $C_{24}H_{14}O_8N_6$ requires C, 56·0 ; H, 2·7%

2-(2 : 4 : 6-*Trinitrostyryl*)-3-*methylquinoxaline* (yield, after 1

hours, 25%) crystallised from *cyclo*hexanol in brown crystals, m. p. 250—251° (decomp.) (Found: C, 53·6; H, 3·0. $C_{17}H_{11}O_6N_5$ requires C, 53·5; H, 2·9%).

2 : 3-*Di*(o-*chlorostyryl*)*quinoxaline* (yield, after 2½ hours, 60%) crystallised from benzene in long, yellow needles, m. p. 189·5° (Found: Cl, 17·5. $C_{24}H_{16}N_2Cl_2$ requires Cl, 17·6%). A careful search gave no indication of the presence of any monostyryl derivative among the products of this reaction.

2 : 3-*Di*(m-*chlorostyryl*)*quinoxaline* (yield, after 5 hours, 30%) was obtained solid with difficulty; the product was distilled in steam, purified by means of ethyl alcohol, and crystallised from light petroleum, forming yellow needles, m. p. 149° (Found: Cl, 17·5%).

2 : 3-*Di*(p-*chlorostyryl*)*quinoxaline* (yield, after 2½ hours, 60%) crystallised from benzene in small, star-shaped clusters of needles, m. p. 218° (Found: Cl, 17·4%).

2 : 3-*Di*(o-*iodostyryl*)*quinoxaline* (yield, after 5 hours, 40%) crystallised from light petroleum (b. p. 90—120°) in pale yellow plates, m. p. 179° (Found: I, 43·4. $C_{24}H_{16}N_2I_2$ requires I, 43·3%).

No crystalline product was isolated when condensations were attempted between 2 : 3-dimethylquinoxaline and dimethylamino-benzaldehyde, chloral, cinnamaldehyde, phenylacetaldehyde, benzil, glyoxal, phthalic anhydride, *p*-nitrosodimethylaniline, Michler's hydrol, or xanthydrol.

Condensation of 2 : 3 : 6-*Trimethylquinoxaline with Aldehydes*.— The base was boiled with benzaldehyde in excess for 2 hours; 2 : 3-*distyryl-6-methylquinoxaline* crystallised from the cooled reaction mixture (yield, 81%) and by recrystallisation from xylene was obtained in small, yellow needles, m. p. 193° (Found: N, 8·3. $C_{25}H_{10}N_2$ requires N, 8·3%).

The following condensations were carried out in acetic anhydride, and the products worked up as described on p. 1968.

2 : 3-*Di*(*methylenedioxystyryl*)-6-*methylquinoxaline* (yield, after 4 hours, 10%) was crystallised from dilute alcohol; m. p. 168° (Found: N, 6·6. $C_{27}H_{20}O_4N_2$ requires N, 6·4%).

2-p-*Methoxystyryl*-3 : 6-*dimethylquinoxaline* (yield, after 5 hours, 1—2%) separated from methyl alcohol in small yellow crystals, m. p. 116° (Found: N, 9·8. $C_{19}H_{18}ON_2$ requires N, 9·7%), and 2 : 3-*di*(p-*methoxystyryl*)-6-*methylquinoxaline* (yield, after 10 hours, 15%) in yellow needles, m. p. 136° (Found: N, 7·1. $C_{27}H_{24}O_2N_2$ requires N, 6·9%).

2 : 3-*Di*(3 : 4-*dimethoxystyryl*)-6-*methylquinoxaline* (yield, after 5 hours, 5%) separated from light petroleum (b. p. 90—120°) in orange-yellow crystals, m. p. 205° (Found: N, 6·1. $C_{29}H_{28}O_4N_2$ requires N, 6·0%).

In the following preparations steam distillation was dispensed with, as the product crystallised from the cooling reaction mixture.

The product from *m*-nitrobenzaldehyde (after 5 hours' heating) was separated into two portions by means of benzene. The less soluble portion was 2 : 3-*di*(m-*nitrostyryl*)-6-*methylquinoxaline*, which was crystallised from *cyclo*hexanol; m. p. 244·5° (yield, 10%) (Found: N, 12·9. $C_{25}H_{18}O_2N_4$ requires N, 12·8%). The more soluble portion was 2-m-*nitrostyryl*-3 : 6-*dimethylquinoxaline* and was crystallised from light petroleum; m. p. 165° (yield, 1—2%) (Found: N, 13·5. $C_{18}H_{15}O_2N_3$ requires N, 13·8%).

2 : 3-*Di*(2 : 4-*dinitrostyryl*)-6-*methylquinoxaline* (yield, after 1¼ hours, 80%) separated from *cyclo*hexanol in orange-yellow crystals, m. p. 251—255° (decomp.) (Found: C, 57·0; H, 3·4; N, 15·7. $C_{25}H_{16}O_8N_6$ requires C, 56·75; H, 3·0; N, 15·9%).

Condensation of 3-Phenyl-2-methylquinoxaline with Aldehydes.— The base was heated with boiling benzaldehyde (4 mols.) for 1 hour. 2-*Styryl*-3-*phenylquinoxaline* crystallised as the mixture cooled (yield, 90%) and separated, on recrystallisation from ethyl alcohol, in pale yellow needles, m. p. 149° (Found: N, 9·3. $C_{22}H_{16}N_2$ requires N, 9·1%).

2-p-*Nitrostyryl*-3-*phenylquinoxaline* was prepared from the base and *p*-nitrobenzaldehyde in acetic anhydride (yield, after 2 hours, 80%). It crystallised from benzene–light petroleum in bright yellow needles, m. p. 233° (Found: N, 12·1. $C_{22}H_{15}O_2N_3$ requires N, 11·9%).

2-(2 : 4-*Dinitrostyryl*)-3-*phenylquinoxaline* (yield, 90%) separated from light petroleum in yellow needles, m. p. 215° (Found: N, 14·1. $C_{22}H_{14}O_4N_4$ requires N, 14·1%).

Behaviour of Phenylbenzylquinoxaline with Aldehydes.—The substances were recovered unchanged when 3-phenyl-2-benzylquinoxaline and *p*-nitrobenzaldehyde; 3-phenyl-2-*p*-methoxybenzylquinoxaline and *p*-nitro- or 2 : 4-dinitro-benzaldehyde; 3-phenyl-2-*p*-chlorobenzylquinoxaline and *p*-nitro- or 2 : 4-dinitro-benzaldehyde or dimethylaminobenzaldehyde were heated together for 6—10 hours in boiling acetic anhydride. The phenylchlorobenzylquinoxaline was unaffected by boiling with benzaldehyde for 3 hours.

Condensation of 2-Benzylquinoxaline with Aldehydes.—The crude benzylquinoxaline was heated with an excess of *p*-nitrobenzaldehyde in boiling acetic anhydride for 5 hours.

2-(β-*Phenyl*-p-*nitrostyryl*)*quinoxaline* separated from the coolin mixture (yield, 1·2 g. from 1·4 g. of benzylglyoxal). It crystallise from ethyl alcohol in pale yellow needles, m. p. 149° (Found: N 12·0. $C_{22}H_{15}O_2N_3$ requires N, 11·9%).

Condensation of the crude base with dinitrobenzaldehyde (7 hour

heating) yielded a trace of a crystalline product, m. p. 261—262°, which was insufficient for analysis, but was probably the corresponding 2-(β-*phenyl*-2 : 4-*dinitrostyryl*)*quinoxaline*.

*Condensation of Quinoxalino*cyclo*pentane with Aldehydes.*—Quinoxalinocyclopentane was converted by heating in boiling benzaldehyde for 2 hours into the *dibenzylidene* derivative (yield, 40%), brownish crystals, m. p. 213°, from ethyl alcohol (Found: N, 8·4. $C_{25}H_{18}N_2$ requires N, 8·1%), and by heating with *p*-nitrobenzaldehyde in acetic anhydride into the *di*-p-*nitrobenzylidene* derivative (yield, after 1 hour, 85%), which crystallised from hot nitrobenzene in yellow needles, decomp. 268—270° (Found: N, 12·8. $C_{25}H_{16}O_4N_4$ requires N, 12·8%). This base also condensed rapidly with 2 : 4-dinitrobenzaldehyde, but the product was so insoluble that it was impossible to purify it.

Condensation of Some Quinoline Bases with 2 : 4-*Dinitrobenzaldehyde.*—The products were obtained crystalline in 60—80% yield in 1—2 hours' heating. Quinaldine yielded 2-(2 : 4-*dinitrostyryl*)-*quinoline*, crystallising from benzene in pale yellow needles, m. p. 200° (Found: N, 13·1. $C_{17}H_{11}O_4N_3$ requires N, 13·1%). 2 : 8-Dimethylquinoline was converted into 2-(2 : 4-*dinitrostyryl*)-8-*methylquinoline*, crystallising from benzene in bright yellow needles, m. p. 198° (Found: C, 64·5; H, 4·5. $C_{18}H_{13}O_4N_3$ requires C, 64·5; H, 3·9%). 2 : 3-Dimethylquinoline gave 2-(2 : 4-*dinitrostyryl*)-3-*methylquinoline*, crystallising from benzene in brown needles, m. p. 257° (Found: C, 64·6; H, 3·7%). The same base, heated in excess of benzaldehyde at 150—160° for 6 hours, was converted into 2-*styryl*-3-*methylquinoline*, which separated as almost colourless crystals, m. p. 102°, from light petroleum (yield, 50%) (Found: C, 88·2; H, 6·4. $C_{18}H_{15}N$ requires C, 88·2; H, 6·1%).

Condensation of 2 : 3-*Dimethylquinoxaline with Ethyl Oxalate.*—To a suspension of sodium ethoxide (2 mols.) in dry ether, mixed with a little xylene, was added an ethereal solution of 2 : 3-dimethylquinoxaline (1 mol.) and ethyl oxalate (2 mols.). At the end of 12 hours a pale yellow colour had developed and traces of a solid were to be seen separating. After 4 weeks, the accumulated solid was collected and washed thoroughly with dry ether. It crystallised from acetic acid or ethyl alcohol in orange-yellow needles, m. p. 129° (yield, 2·5 g. from 4·7 g. of base). This was *ethyl* 2-*methylquinoxaline*-3-*pyruvate* (Found: C, 65·6; H, 5·5. $C_{14}H_{14}O_3N_2$ requires C, 65·2; H, 5·5%). When potassium ethoxide was substituted for sodium ethoxide in the preparation (compare Wislicenus, *Ber.*, 1909, **42**, 1140), the yield was improved (3·2 g. from 4·7 g. of base). The p-*nitrophenylhydrazone* crystallised in orange needles, m. p. 189°, from ethyl alcohol (Found: N, 18·0. $C_{20}H_{19}O_4N_5$ requires N, 17·8%).

After dimethylquinoxaline had been kept with amyl nitrite and sodium or potassium ethoxide for 12 days, no condensation product could be detected.

Bromination of the Quinoxaline Bases.—2-Methylquinoxaline, brominated as described by Hammick (J., 1923, **123**, 2883), yielded an oil which solidified 2 days later. After several recrystallisations from ethyl alcohol, 2-ω-*tribromomethylquinoxaline* was obtained (yield of pure substance, 10%) in pink plates, m. p. 109° (Found: Br, 62·7. $C_9H_5N_2Br_3$ requires Br, 63·0%).

2 : 3-Dimethylquinoxaline, brominated with 6 molecular proportions of bromine under similar conditions, gave a quantitative yield of 2 : 3-*di*(ω-*dibromomethyl*)*quinoxaline*, which crystallised from glacial acetic acid in colourless needles, m. p. 228° (Found: Br, 66·9. $C_{10}H_6N_2Br_4$ requires Br, 66·95%). This substance was recovered unchanged after boiling in glacial acetic acid for 1 hour with a large excess of bromine. When this compound was boiled in glacial acetic acid solution with silver acetate, the halogen was removed. The resulting solution gave a precipitate with *p*-nitrophenylhydrazine which was sparingly soluble in the common solvents and could not be obtained pure. The di-aldehyde was too unstable to be isolated by evaporation even under reduced pressure in an inert atmosphere.

Bromination of 3-phenyl-2-methylquinoxaline gave 3-*phenyl*-2-ω-*dibromomethylquinoxaline* (yield, 90%), which separated from light petroleum in clusters of needles, m. p. 148° (Found: Br, 42·1. $C_{15}H_{10}N_2Br_2$ requires Br, 42·25%).

To 3-phenyl-2-benzylquinoxaline (1·5 g.), dissolved in glacial acetic acid containing sodium acetate (2·3 g.), was added bromine (1·5 g.; 2 mols.) in a little acetic acid at 70°. After the reaction had been completed on the water-bath, the product obtained on pouring the mixture into water proved to be 3-*phenyl*-2-*phenylacetoxymethylquinoxaline* (yield, 90%), which crystallised from light petroleum in colourless prisms, m. p. 126°. It was free from halogen and after hydrolysis gave a test for acetic acid (Found: C, 78·3; H, 5·3 $C_{23}H_{18}O_2N_2$ requires C, 78·0; H, 5·1%).

3-Phenyl-2-*p*-chlorobenzylquinoxaline underwent a simila change with bromine and sodium acetate in glacial acetic aci solution, giving in quantitative yield the bromine-free produc 3-*phenyl*-2-p-*chlorophenylacetoxymethylquinoxaline*, colourless prism from light petroleum, m. p. 119° (Found: Cl, 9·4. $C_{23}H_{17}O_2N_2$(requires Cl, 9·1%).

3-Phenyl-2-*p*-methoxybenzylquinoxaline did not react wit bromine under similar conditions to the above, nor when the reactic mixture was boiled for 1 hour.

Action of Methyl Iodide on Dimethylquinoxaline.—When 2 : 3-c

methylquinoxaline was heated at various temperatures with methyl iodide (2 or 3 mols.), no crystalline product could be isolated, nor could the methosulphate be obtained by means of methyl sulphate. However, the base, heated in a sealed tube at 90° for 6½ hours with methyl iodide (10 mols.), furnished a *monomethiodide* (yield, 80%) which crystallised from ethyl alcohol in greenish-yellow needles, m. p. 192° (Found : I, 42·6. $C_{11}H_{13}N_2I$ requires I, 42·4%). Addition of sodium hydroxide to the aqueous solution precipitated an oil which could not be obtained crystalline.

The methiodide was boiled in ethyl alcohol with benzaldehyde or nitrosodimethylaniline and a trace of piperidine. In each case a brilliant colour change occurred and a black solid was precipitated, which, however, was insoluble in all solvents including phenol, nitrobenzene, *cyclo*hexanone, and acetic acid.

We are indebted to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this investigation.

THE UNIVERSITY, SHEFFIELD. [*Received, May 14th*, 1928.]

CCLVIII.—*The Relative Reactivity of Methylene Groups in* 1 : 3-*Diketones.*

By ARTHUR BERTRAM EDMUND LOVETT and ELWYN ROBERTS.

THE present investigation was designed to discover which methylene group, in a diketone of the general formula $CH_2R{\cdot}CO{\cdot}CH_2{\cdot}COR'$, would be the more reactive as regards condensation with aldehydes. Bülow and Grotowsky (*Ber.*, 1901, **34**, 1479) assumed that in ω-phenylacetylacetophenone, $CH_2Ph{\cdot}CO{\cdot}CH_2{\cdot}COPh$, the methylene group adjacent to the benzoyl radical was the more reactive towards nitrous acid and diazo-compounds. Different aldehydes, however, behave very differently towards phenylacetylacetophenone in presence of piperidine; for instance, benzaldehyde and cinnamaldehyde give resins, but salicylaldehyde readily condenses in alcohol or benzene solution. Since the resulting o-*hydroxybenzylidenephenylacetylacetophenone* is readily convertible, in good yield, into acetophenone and 3-phenylcoumarin, it must have the formula $OH{\cdot}C_6H_4{\cdot}CH{:}CPh{\cdot}CO{\cdot}CH_2{\cdot}COPh$, and not

$$OH{\cdot}C_6H_4{\cdot}CH{:}C(COPh){\cdot}CO{\cdot}CH_2Ph.$$

The more reactive methylene group in ω-phenylacetylacetophenone is therefore that adjacent to the phenyl group. The formation of 3-phenylcoumarin cannot be attributed to an initial hydrolysis

giving rise to phenylacetic acid and acetophenone, since phenylacetic acid does not condense with salicylaldehyde under the same conditions to give the coumarin. Furthermore, the intermediate product on continued recrystallisation from a non-aqueous solvent such as benzene gives a mixture in which 3-phenylcoumarin increasingly preponderates. It reacts with concentrated sulphuric acid and acetic anhydride to give products of undetermined constitution.

5-Methyl, 5-chloro-, 5-bromo-, 5-nitro-, 3-nitro-, 3 : 5-dichloro-, 3 : 5-dibromo-, and 3-nitro-5-methyl-salicylaldehydes condense with ω-phenylacetylacetophenone under similar conditions to give substituted 3-phenylcoumarins, but in no case could the intermediate product be isolated. The yield of coumarin, except from salicylaldehyde and its 5-methyl derivative, was small, indicating the influence of substituents on the condensation. From 5-bromo-3-nitrosalicylaldehyde a trace only of the coumarin, and from 5-chloro-3-nitro- and 3 : 5-dinitro-salicylaldehydes no coumarin was obtained; these three aldehydes react with piperidine to give stable piperidides of undetermined constitution. Phenylacetylacetophenone and 2-hydroxy-α-naphthaldehyde in the presence of piperidine give, not the expected 3-phenylbenzcoumarin, but a red compound probably having formula $C_{27}H_{18}O_2$. 2-Hydroxy-α-naphthaldehyde, however, condenses with ethyl acetoacetate to give 3-acetobenzcoumarin (Knoevenagel and Schrötter, *Ber.*, 1904, **37**, 4484; compare Bülow and Grotowsky, *Ber.*, 1902, **35**, 1803).

ω-Propionyl- and butyryl-acetophenones and propionylacetone were condensed with salicylaldehyde and substituted salicylaldehydes in the presence of piperidine. Resin-like products were obtained from which no crystalline solid could be isolated. The effect of the nature of the groups R, R′ on the reactivity of the methylene groups could not therefore be readily determined by this method.

In all cases the coumarins were synthesised for identification purposes by the Perkin reaction. The yield of coumarin by this method was good, in contradistinction to the poor yields obtained by condensation of aldehyde and ketone.

EXPERIMENTAL.

ω-Phenylacetyl-, propionyl-, and butyryl-acetophenones and propionyl-acetone were prepared by a modification of Claisen's method, a suspension of powdered sodium in xylene being used instead of anhydrous sodium ethoxide.

Propionylacetophenone.—The green copper salt crystallised from acetone in needles, m. p. 151—152°. The pure ketone boils

149°/17 mm. or 151°/19 mm. Beyer and Claisen (*Ber.*, 1887, **20**, 2178) give b. p. 170—172°/30—31 mm.

The p-*nitrophenylhydrazone* was obtained by heating 1·76 g. (1 mol.) of the ketone and 1·53 g. (1 mol.) of *p*-nitrophenylhydrazine at 100° for 7 hours. The product, a thick gum, when covered with 96% alcohol and kept for 3 days, set to a solid mass. It was crystallised from aqueous alcohol, in which it was fairly easily soluble, and then from light petroleum (b. p. 80—100°), fine yellow needles (1·3 g.), m. p. 67—68°, being obtained (Found: N, 13·4. $C_{17}H_{17}O_3N_3$ requires N, 13·5%).

Propionylacetophenoneanil.—A mixture of 5 g. (1 mol.) of the ketone and 2·64 g. (1 mol.) of freshly distilled aniline was heated under reflux for ½ hour; no more water then appeared to separate. Benzene extracted from the product a dark brown, mobile oil which deposited a solid after a few days. This, after being pressed on porous porcelain, crystallised from light petroleum (b. p. 40—60°), in which it was readily soluble, in prisms (1·8 g.), m. p. 48—49° (Found: N, 5·7. $C_{17}H_{17}ON$ requires N, 5·6%).

Condensation of Salicylaldehydes with ω-Phenylacetylacetophenone.—A solution of salicylaldehyde (7·5 g.; 1 mol.) and phenylacetylacetophenone (14·6 g.; 1 mol.) in 25 c.c. of absolute alcohol was treated with piperidine (45 drops; which produced a marked development of heat and deepening of colour) and heated on the water-bath; o-*hydroxybenzylidenephenylacetylacetophenone* separated in prisms from the hot liquor. The latter was decanted, and the solid washed with alcohol and collected (13·3 g.; m. p. 171—174°) (Found: C, 80·6; H, 5·3. $C_{23}H_{18}O_3$ requires C, 80·7; H, 5·3%). Recrystallisation from alcohol or benzene lowers the melting point. The yield of product depends upon the amount of piperidine used, the above quantity giving the maximum yield.

The mother-liquor was heated on the water-bath for a further hour; 3-phenylcoumarin (2·4 g.) separated on cooling.

If the intermediate product was not isolated, it gradually dissolved on prolonged heating (5 hours); on cooling, almost pure 3-phenylcoumarin (7·0 g.) separated, m. p. 140—141° (Found: C, 81·1; H, 4·5. Calc.: C, 81·1; H, 4·5%).

The same products were obtained on varying the molecular proportion of aldehyde and ketone.

Ethyl phenylacetate (1 mol.) and salicylaldehyde (1 mol.), on heating on the water-bath for 4 hours in presence of piperidine, gave a 16% yield of pure 3-phenylcoumarin.

In the condensations of ω-phenylacetylacetophenone and substituted *o*-hydroxyaldehydes the same method was employed, the period of heating varying from 7 to 11 hours. In some cases the

coumarin was deposited from the hot solution. Unless otherwise stated in the following table, the coumarin was crystallised from alcohol, in which it was very sparingly soluble. The yields obtained (I) by ketone condensation and (II) by the Perkin reaction are given.

Substituted 3-phenyl-coumarin.	Form.	M. p.	% found.	% calc.	Yield. (I).	(II).
6-*Chloro-*	Pale yellow prisms	199°	Cl, 14·3	13·8	25	40
6-*Bromo-*	,,	189—191	Br, 26·6	26·5	25	62
6-*Nitro-*	Yellow prisms	251—253	N, 5·3	5·3	4	60
6-*Methyl-*	Pale yellow needles	146—147·5	C, 80·2; H, 5·1	80·4; 5·1	42	40
8-*Nitro-*	,,	236—239	N, 5·3	5·3	4	65
6 : 8-*Dichloro-* ...	Colourless needles *	193—194·5	Cl, 24·5	24·5	16	27
6 : 8-*Dibromo-* ...	,, *	186—187·5	Br, 42·3	42·1	trace	30
6 : 8-*Dinitro-*	Pale yellow needles *	244—246	N, 8·9	9·0	0	60
6-*Chloro*-8(?)-*nitro-*	Yellow needles	212—214	Cl, 11·6	11·7	0	70
6-*Bromo-8-nitro-*	Plates †	228—230	Br, 22·8	23·1	trace	74
8-*Nitro-6-methyl-*	Yellow needles	180—182	N, 5·0	5·0	12·5	44

* From acetic acid. † From acetic anhydride.

3 : 5-*Dinitrosalicylaldehyde*.—The mixture of 3- and 5-nitro-salicylaldehydes (33 g.) obtained by the nitration of salicylaldehyde (von Miller, *Ber.*, 1887, **20**, 1927) was added cautiously, with cooling in ice and salt, to a mixture (100 g.) of concentrated sulphuric acid (2 parts) and nitric acid (*d* 1·5; 1 part). After 30 minutes the nitration mixture was poured on ice, and the yellow product was washed with ice-water, dried, and crystallised three times from benzene, giving lemon-yellow prisms (20 g.), m. p. 58—60° (Found N, 13·1. $C_7H_4O_6N_2$ requires N, 13·2%). Its *constitution* was proved by oxidising it by alkaline permanganate to 3 : 5-dinitro-salicylic acid.

5-*Chloro*-3(?)-*nitrosalicylaldehyde*.—A solution of 8·1 g. of 5-chloro-salicylaldehyde in 100 c.c. of glacial acetic acid was slowly treated at 60—70° with nitric acid (*d* 1·42; 8 c.c.). The solution was then cooled slowly, the yellow, crystalline product removed, the filtrate diluted with 100 c.c. of water, and the precipitated solid collected. The combined product was crystallised twice from light petroleum (b. p. 80—100°), from which it separated in yellow needles (5·5 g., m. p. 105—107° (Found : Cl, 17·4. $C_7H_4O_4NCl$ requires Cl, 17·6%). The constitution of this aldehyde was inferred by analogy, since 5-bromosalicylaldehyde nitrates under identical conditions (v. Auwers and Bürger, *Ber.*, 1898, **31**, 3934) to give 5-bromo-3-nitro-salicylaldehyde.

Condensation of 2-Hydroxy-α-naphthaldehyde and ω-Phenylacetylacetophenone.—A solution of 2·4 g. (1 mol.) of the ketone, 1·7 g. (1 mol.) of the aldehyde, and 7 drops of piperidine in 5 c.c

absolute alcohol was heated on the water-bath for 2 hours. On cooling, no separation of solid occurred. The mixture was then heated for a further 9 hours; on cooling, a red crystalline mass was now obtained. After being washed with spirit, this crystallised from alcohol, in which it was very sparingly soluble (1 g. in 200 c.c.), in small, deep blood-red prisms (0·9 g.), m. p. 155—156·5° (Found: C, 86·8; H, 4·9. $C_{27}H_{18}O_2$ requires C, 86·6; H, 4·8%).

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EAST LONDON COLLEGE,
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CCLIX.—*The Mechanism of Tautomeric Interchange and the Effect of Structure on Mobility and Equilibrium. Part III. The Function of Alkaline and Acid Catalysts in the Mutarotation of some Derivatives of Tetramethyl Glucose.*

By JOHN WILLIAM BAKER.

IN Part II (this vol., p. 1583) it was shown that catalysts which facilitate the prototropic change involved in the mutarotation of sugars may be of two kinds: (*a*) those which attack the ionising proton directly, and (*b*) those which facilitate its liberation indirectly. Experiments on the relative velocity of mutarotation of a series of nitrogen derivatives of tetra-acetyl glucose of type I (X = Ac) suggested that acids, which fall within the second category

$$\underset{\llcorner[(CH\cdot OX)_3]\lrcorner}{RHN—CH——O——CH\cdot CH_2\cdot OX} \qquad (I.)$$

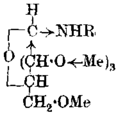
of catalysts, function by inducing a positive charge on the nitrogen atom, which in turn facilitates the liberation of the attached proton. Unfortunately, in this series of sugar derivatives a study of the action of catalysts of the first type, of which alkalis are an example, is rendered difficult by the tendency of the acetyl groups to hydrolysis. Such an investigation is, however, possible in the case of the corresponding derivatives of tetramethyl glucose, and this communication deals with the effect of acid and alkaline catalysts on the relative velocities of mutarotation of a series of *p*-substituted anilides of tetramethyl glucose (type I, X = Me) (prepared by the direct interaction of the sugar and the base) when

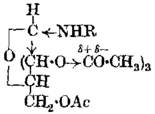
the group R is varied. With acid catalysts, it is again found, as is the case in the corresponding tetra-acetyl derivatives, that, as the group R is varied, the velocity of the mutarotation runs parallel with the strengths as bases of the compounds RNH_2, *viz.*,

$$-C_6H_4{\cdot}OMe(p) > -C_6H_4Me(p) > -C_6H_5 > -C_6H_4Cl(p) > -C_6H_4Br(p)$$

a sequence which is in agreement with the prediction based on the mechanism previously suggested, but opposed to that required by the extension of a duplex theory (Part II, *loc. cit.*).

The solvent * used was one in which a determination of the velocities of mutarotation of three of the corresponding derivatives of tetra-acetyl glucose had already been made, and hence data are now available for a comparison of the effect, on the velocity of mutarotation, of structural changes in the non-tautomeric glucose portion of the molecule. By analogy with the known effect of the acetyl group in diminishing, and of the methyl group in increasing, the basic character of the nitrogen atom in $NHR{\rightarrow}\overset{\delta+\delta-}{CO}{\cdot}CH_3$ and $NHR{\leftarrow}Me$, it would be expected that the anilides of tetramethyl glucose (A) would be more basic in character than the corresponding derivatives of tetra-acetyl glucose (B),

(A.) 

 (B.)

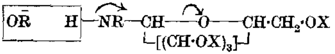
and hence, under identical conditions of acid catalysis, the velocity of mutarotation of derivatives of the former should be greater than that of corresponding derivatives of the latter. The experimental results given below, which refer to the velocity of mutarotation in a 0·9*N*-solution of acetic acid in ethyl acetate at 25°, are in agreement with this prediction.

Mutarotation of p-*substituted anilides in* 0·9N-*acetic acid in ethy acetate at* 25°.

R.	Unimolecular velocity coefficient (hr.$^{-1}$). (*a*) Derivatives of tetramethyl glucose.	(*b*) Derivatives of tetra-acetyl glucose.
C_6H_4Br	0·39	—
C_6H_4Cl	0·46	—
C_6H_5	1·30	0·21
C_6H_4Me	4·12	0·58
$C_6H_4{\cdot}OMe$	12·0	1·69

* Pure, acid-free ethyl acetate (but not an arrest sample) was used in t preparation of the solution; but the *same* solution was used throughou since the object was merely to obtain constant catalytic conditions.

The results obtained for alkaline catalysis are more complicated and their interpretation much less clearly defined than in the case of acid catalysis. It would be expected that the primary function of alkaline catalysts, which are included in the first class, would be the direct attack of the ionising proton of the sugar molecule by the negative ion of the catalyst in accordance with the scheme



Other structural and experimental conditions being equal, the velocity of mutarotation based on this mechanism will depend on the relative ease with which the H of the -NHR group can separate as a proton. This, in turn, as indicated in Part II, will depend on the extent to which the group R collaborates with the catalyst proton acceptor. Approximate data of the order of this effect may be obtained from the relative strengths as acids of the compounds $R \cdot CO_2H$ or $R \cdot OH$. This for the series of *p*-substituted anilides studied is

$$(-C_6H_4Br, -C_6H_4Cl) > -C_6H_5 > -C_6H_4Me > -C_6H_4 \cdot OMe.$$

On the other hand, experimentally it is difficult completely to eliminate catalysts of the second type, such as water and possibly alcohol, which may function in an indirect manner by a mechanism analogous to that shown to exist in the case of catalysis by acids, *viz.*, by inducing a fractional positive charge on the nitrogen atom. Such catalytic action would be most effective with the derivative of the strongest base, the sequence in the series under consideration being that given for acid catalysis on p. 1980. Therefore in alkaline catalysis it seems probable that at least two different types of mechanism may function, one of which is most powerful with the derivative of the weakest base, the other reaching its maximum with the derivative of the strongest base. The superimposition of these two mechanisms may therefore lead to the existence of a minimum value for the velocity of mutarotation at some intermediate point in the series. This theory is tentatively suggested as one satisfactory explanation of the experimental results obtained. These refer to the mutarotation of a series of *p*-substituted anilides of tetramethyl glucose in ether containing a small concentration of an alcoholic solution of sodium ethoxide. In the first two series of experiments, the concentration of sodium ethoxide was approximately $0 \cdot 0006N$, and a small (constant but undetermined) quantity of water was present. The values of the unimolecular velocity coefficients of the various derivatives at 25° are as follows: $-C_6H_4Cl$, 1·33; $-C_6H_4Br$, 1·24; $-C_6H_5$, 1·13 (minimum); $-C_6H_4Me$, 1·21; $-C_6H_4 \cdot OMe$,

2·41 (hr.$^{-1}$). In this series a minimum value for the velocity coefficient is found in the case of the unsubstituted anilide.

With the object of accelerating the direct mechanism and impeding the indirect type of catalytic action, another series of experiments was carried out in which a higher proportion (0·001N) of sodium ethoxide was used, and in which water was rigidly excluded. These measures were calculated to shift the position of the minimum velocity to the right in the above series, so that a greater number of the derivatives would fall into the sequence demanded by the direct mechanism alone (p. 1981). The following experimental values of the unimolecular velocity coefficients confirm this expectation:

$-C_6H_4Cl$, 11·4; $-C_6H_4Br$, 9·1; $-C_6H_5$, 7·7; $-C_6H_4Me$, 6·1 (minimum); $-C_6H_5{\cdot}OMe$, 14·7.

EXPERIMENTAL.

I. *Preparation of p-Substituted Anilides of Tetramethyl Glucose.*—These were prepared by boiling a mixture of tetramethyl glucose with an excess of the appropriate base in alcoholic solution for several hours in accordance with the method used by Irvine and Gilmour (J., 1908, **93**, 1440) for the preparation of the anilide.

p-*Bromoanilide*, after crystallisation from methyl alcohol, has m. p. 154° (Found: C, 48·8; H, 6·1. $C_{16}H_{24}O_5NBr$ requires C, 49·2; H, 6·2%).

p-*Chloroanilide*, after crystallisation from methyl alcohol–ligroin (b. p. 60—80°), has m. p. 141° (Found: C, 55·3; H, 7·0. $C_{16}H_{24}O_5NCl$ requires C, 55·5; H, 7·0%).

p-*Toluidide*, after crystallisation from absolute alcohol, has m. p. 151° (Found: C, 62·7; H, 8·0. $C_{17}H_{27}O_5N$ requires C, 62·8; H, 8·4%).

p-*Anisidide*, after crystallisation from ether–ligroin (b. p. 40—60°), has m. p. 110° (Found: C, 59·8; H, 8·0. $C_{17}H_{27}O_6N$ requires C, 59·8; H, 8·0%).

The anilide had m. p. 135° (Found: C, 61·7; H, 8·0. Calc.: C, 61·7; H, 8·1%).

II. *Relative Velocity Experiments.*—(A) *With acid catalysts.* The solution employed was one previously used in the determination of the relative velocities of mutarotation of the corresponding derivatives of tetra-acetyl glucose, and consisted of pure ethyl acetate to which acetic acid in a concentration 0·9N had been added (see footnote, p. 1980).

All polarimetric measurements were carried out in a 2-dcm. silica polarimeter tube with optically ground silica endplates fused on. The tube was jacketed for temperature control, the temperature

readings recorded being those of the jacket. Measurements were made on the mercury green line, the light source being a powerful Kelvin, Bottomley, and Baird mercury vapour lamp. The velocity determinations were carried out consecutively, each series being completed within a few days in order to avoid any possibility of change in the composition of the solvent during a series of comparative experiments.

The value of $[\alpha]_0$ was determined by extrapolation to zero time of the straight line obtained by plotting $\log([\alpha]_0 - [\alpha]_\infty)$ against time. Details of the polarimetric measurements are given only in the first set of each series.

Mutarotation of tetramethyl glucose anilides in a 0·9N-solution of acetic acid in ethyl acetate at 25°.

(*a*) p-Bromoanilide. Strength of solution = 0·9856 g./100 c.c. (0·025 g.-mol./l.).

$$[\alpha]_D = 245°. \quad k = \frac{2\cdot3}{t}\log\frac{[\alpha]_\infty - [\alpha]_0}{[\alpha]_\infty - [\alpha]_t}(\text{hr.}^{-1}).$$

t (hrs.).	*a*.	$[\alpha]_{5461}$.	*k*.	*t* (hrs.).	*a*.	$[\alpha]_{5461}$.	*k*.
0·084	4·73°	240·0°	0·384	1·75	3·33°	168·9°	0·405
0·166	4·64	235·4	0·388	2·25	3·07	155·8	0·402
0·25	4·55	230·8	0·386	3·34	2·66	135·0	0·397
0·417	4·36	221·2	0·408	4·0	2·49	126·3	0·393
0·50	4·28	217·1	0·409	5·25	2·25	114·2	0·394
0·75	4·09	207·5	0·380	6·34	2·09	106·0	—
1·0	3·89	197·3	0·382	8·17	1·99	101·0	—
1·25	3·68	186·7	0·392	11·75	1·88	95·4	—
1·50	3·51	178·1	0·392	∞	1·88	95·4	—
						Mean	0·394

(*b*) p-*Chloroanilide*. Strength of solution, 0·8656 g./100 c.c. (0·025 g.-mol./l.). $[\alpha]_0 = 268°$. $[\alpha]_\infty = 100·5°$.

Mean value of *k* (12 observations) = 0·464 hr.$^{-1}$ (max., 0·485; min., 0·445).

(*c*) *Anilide*. Strength of solution, 0·7808 g./100 c.c. (0·025 g.-mol./l.). $[\alpha]_0 = 285°$. $[\alpha]_\infty = 106°$.

Mean value of *k* (10 observations) = 1·30 hr.$^{-1}$ (max., 1·37; min., 1·25).

(*d*) p-*Toluidide*. Strength of solution, 0·8256 g./100 c.c. (0·025 g.-mol./l.). $[\alpha]_0 = 272°$. $[\alpha]_\infty = 110°$.

Mean value of *k* (11 observations) = 4·12 hr.$^{-1}$ (max., 4·18; min., 4·04).

(*e*) p-*Anisidide*. Strength of solution, 0·7408 g./100 c.c. (0·025 g.-mol./l.). $[\alpha]_0 = 279°$. $[\alpha]_\infty = 107°$.

Mean value of *k* (8 observations) = 12·1 hr.$^{-1}$ (max., 12·8; min., 11·6).

Summary of Acid Catalysis.

p-Substituent.	No. of mols. of anilide per litre.	Dissociation constant, K_b, of p-substituted aniline as a base.	Unimolecular velocity coefficient, k.	k/K_b.
Br	0·025	$1·0 \times 10^{-10}$	0·39	$0·39 \times 10^{10}$
Cl	,,	$1·5 \times 10^{-10}$	0·46	$0·31 \times 10^{10}$
H	,,	$4·6 \times 10^{-10}$	1·30	$0·28 \times 10^{10}$
Me	,,	$11—15 \times 10^{-10}$	4·12	$0·38 \times 10^{10}$
OMe	,,	15×10^{-10}	12·1	$0·77 \times 10^{10}$

(B) *With alkaline catalysts. Series I and II.*

Preparation of solution. A 0·1*N*-solution of sodium ethoxide in alcohol was prepared by addition of the required quantity of sodium to absolute alcohol (calcium-dried). 1·5 C.c. of this solution were added to about 246 c.c. of sodium-dried ether, and the solution made up to 250 c.c. by addition of ordinary absolute alcohol (99·5%) to keep the sodium ethoxide in solution. The solution was therefore approximately 0·0006*N* in sodium ethoxide.

Mutarotation of tetramethyl glucose anilides in an approximately 0·0006N-solution of sodium ethoxide in ether at 25°.

(*a*) *Anilide.* Strength of solution = 0·9976 g./100 c.c. $[\alpha]_0 = 274°$. $[\alpha]_\infty = 163°$. $k = \frac{2·3}{t} \log \frac{[\alpha]_\infty - [\alpha]_0}{[\alpha]_\infty - [\alpha]_t}$.

t (hrs.).	α.	$[\alpha]_{5461}$.	k.	t (hrs.).	α.	$[\alpha]_{5461}$.	k.
0·067	5·32°	266·6°	1·036	1·17	3·84°	192·5°	1·134
0·167	5·12	256·5	1·033	1·75	3·56	178·4	1·125
0·334	4·78	239·6	1·109	2·25	3·43	171·9	1·106
0·417	4·64	232·6	1·120	3·0	3·33	166·9	—
0·5	4·51	226·0	1·131	6·0	3·25	162·9	—
0·666	4·30	215·6	1·120	∞	3·25	162·9	—
0·75	4·21	211·0	1·116			Mean	1·11

(*b*) p-*Toluidide.* Strength of solution, 0·9872 g./100 c.c. (0·030 g.-mol./l.). $[\alpha]_0 = 249°$. $[\alpha]_\infty = 153°$.

Mean value of *k* (9 observations) = 1·21 hr.$^{-1}$ (max., 1·23 min., 1·17).

(*c*) p-*Bromoanilide.* Strength of solution, 1·000 g./100 c.c. (0·026 g.-mol./l.). $[\alpha]_0 = 239°$. $[\alpha]_\infty = 139°$.

Mean value of *k* (11 observations) = 1·20 hr.$^{-1}$ (max., 1·2[illegible] min., 1·15).

(*d*) p-*Chloroanilide.* Strength of solution, 1·000 g./100 c. (0·029 g.-mol./l.). $[\alpha]_0 = 266°$. $[\alpha]_\infty = 155°$.

Mean value of *k* (10 observations) = 1·32 hr.$^{-1}$ (max., 1·3[illegible] min., 1·29).

(*e*) p-*Anisidide.* Strength of solution, 0·9912 g./100 c.c. (0·029 g.-mol./l.). $[\alpha]_0 = 259°$. $[\alpha]_\infty = 157°$.

Mean value of *k* (9 observations) = 2·37 hr.$^{-1}$ (max., 2·4[illegible] min., 2·29).

This series was repeated in the same solvent after it had remained in the thermostat at 25° for a fortnight. The same *order* of velocities was found, although, probably owing to the slight decrease in the concentration of sodium ethoxide present, the *absolute* values of the velocity coefficients were about 20—30% lower in each case.

(*a*) *Anilide.* Strength of solution, 0·7832 g./100 c.c. (0·025 g.-mol./l.). $[\alpha]_0 = 272°$. $[\alpha]_\infty = 163°$.

Mean value of k (9 observations) = 0·73 hr.$^{-1}$ (max., 0·76; min., 0·71).

(*b*) p-*Toluidide.* Strength of solution, 0·8248 g./100 c.c. (0·025 g.-mol./l.). $[\alpha]_0 = 247°$. $[\alpha]_\infty = 153°$.

Mean value of k (9 observations) = 0·98 hr.$^{-1}$ (max., 1·05; min., 0·93).

(*c*) p-*Bromoanilide.* Strength of solution, 0·9809 g./100 c.c. (0·025 g.-mol./l.). $[\alpha]_0 = 241°$. $[\alpha]_\infty = 139°$.

Mean value of k (10 observations) = 0·80 hr.$^{-1}$ (max., 0·83; min., 0·77).

(*d*) p-*Chloroanilide.* Strength of solution, 0·8704 g./100 c.c. (0·025*N*). $[\alpha]_0 = 267°$. $[\alpha]_\infty = 154°$.

Mean value of k (11 observations) = 1·00 hr.$^{-1}$ (max., 1·04; min., 0·95).

(*e*) p-*Anisidide.* Strength of solution, 0·8704 g./100 c.c. (0·025*N*). $[\alpha]_0 = 251°$. $[\alpha]_\infty = 152°$.

Mean value of k (9 observations) = 2·14 hr.$^{-1}$ (max., 2·31; min., 2·02).

Series III and IV. Velocity of mutarotation of tetramethyl glucose anilides in 0·001N-*sodium ethoxide in ether at 25°.* In the first and preliminary of these two series an approximately 0·001*N*-solution of sodium ethoxide in ether was employed, but a very small (constant) quantity of water was present. The alcohol and ether were both dried over sodium, but the rigid precautions to exclude water taken in the next series were omitted. The results obtained are summarised below.

p-Substituent.	Strength of soln. (g./100 c.c.).	$[\alpha]_0$.	$[\alpha]_\infty$.	Mean value of k * (hr.$^{-1}$) (natural logs).
Br	0·9880	250°	137°	3·5
H	0·9904	296	164	3·5
Me	1·0016	254	161	2·3
OMe..................	1·0016	257	155	6·4

* Obtained graphically from the straight line obtained by plotting t against $\log([\alpha]_0 - [\alpha]_\infty)$.

In the next series, the alcohol used was refluxed over metallic calcium until a large amount of calcium ethoxide was formed; it was then transferred to a dry distillation apparatus closed with

drying-tubes containing phosphoric oxide, and, after 12 hours, distilled directly into a dried burette closed with a drying-tube containing phosphoric oxide. The sample so obtained had $d_4^{18°}$ 0·7909, the value for 100% alcohol given in Landolt-Börnstein's tables being 0·79074 at 18°. The sample therefore contained less than 0·1% of water.

The 0·1*N*-sodium ethoxide solution was prepared by the addition of the calculated quantity of clean dry sodium to the known volume of alcohol in the burette, and 2·5 c.c. of this solution were run directly (avoiding long contact with the air) into about 245 c.c. of ether which had been dried and distilled over sodium. The solutior was made up to 250 c.c. with a few c.c. of the sample of anhydrou alcohol obtained above, and was left tightly stoppered in a ther mostat at 25° overnight before the first set of velocity measurement was taken.

(*a*) p-*Toluidide*. Strength of solution, 0·8256 g./100 c.c. (0·025 g.-mol./l.).

$$[\alpha]_0 = 261°. \quad [\alpha]_\infty = 158°. \quad k = \frac{2\cdot3}{t}\log\frac{[\alpha]_\infty - [\alpha]_0}{[\alpha]_\infty - [\alpha]_t}(\text{hr.}^{-1}).$$

t (hrs.).	α.	$[\alpha]_{5461}$.	k.	t (hrs.).	α.	$[\alpha]_{5461}$.	k.
0·084	3·64°	220·5°	(5·78)	0·28	2·90°	175·6°	5·95
0·117	3·46	209·5	(5·80)	0·33	2·83	171·4	5·99
0·15	3·26	197·4	6·27	0·5	2·69	162·9	6·28
0·167	3·21	194·4	6·12	0·58	2·65	160·4	6·11
0·2	3·10	187·8	6·08	1·25	2·60	157·5	—
0·22	3·04	184·1	6·23	5·7 (∞)	2·60	157·5	—
0·25	2·97	179·9	6·07			Mean	6·12

(*b*) *Anilide*. Strength of solution, 0·7896 g./100 c.c. (0·025 g mol./l.). $[\alpha]_0 = 290°$. $[\alpha]_\infty = 160°$.

Mean value of k (6 observations) = 7·73 hr.$^{-1}$ (max., 7·7 min., 7·63).

(*c*) p-*Bromoanilide*. Strength of solution, 0·9712 g./100 ((0·025 g.-mol./l.). $[\alpha]_0 = 259°$. $[\alpha]_\infty = 142°$.

Mean value of k (7 observations) = 9·14 hr.$^{-1}$ (max., 9· min., 8·70).

(*d*) p-*Chloroanilide*. Strength of solution, 0·8752 g./100 (0·025 g.-mol./l.). $[\alpha]_0 = 270°$. $[\alpha]_\infty = 146°$.

Mean value of k (7 observations) = 11·4 hr.$^{-1}$ (max., 1 min., 10·5).

(*e*) p-*Anisidide*. Strength of solution, 0·8744 g./100 c.c. (0·02 mol./l.). $[\alpha]_0 = 257°$. $[\alpha]_\infty = 145°$.

Mean value of k (6 observations) = 14·7 hr.$^{-1}$ (max., 1 min., 14·0).

Values of $[\alpha]_\infty$ *in Alkaline and Acid Catalysis Experiments*.—I be noticed that the end values obtained in the alkaline cat experiments agree amongst themselves, but are very different

those obtained in acid catalysis. This was shown to be due entirely to the difference in solvents used—ether in the alkaline catalysis and ethyl acetate in the acid catalysis. The final, constant, value of a solution of tetramethyl glucose *p*-toluidide (0·8416 g.) in 100 c.c. of a 0·9*N*-solution of acetic acid in ether was $\alpha = 2{\cdot}60°$, whence $[\alpha]_{5461} = 155°$, in good agreement with the end values obtained for this derivative in the alkaline catalysis experiments, and differing from the value (110°) obtained in a 0·9*N*-solution of acetic acid in ethyl acetate.

The author desires to express his thanks to the Royal Society for a grant with which some of the expense incurred in this investigation has been met.

THE UNIVERSITY, LEEDS. [*Received, May 16th,* 1928.]

NOTES.

The Nature of the Deposit formed during the Electrolysis of Neutral and Alkaline Solutions with an Antimony Cathode. By JULIUS GRANT.

ACCORDING to Weeks and Druce (J., 1925, **127**, 1069) a solid hydride of antimony (Sb_2H_2) is produced when stibine is passed into a concentrated solution of sodium hydroxide, and the black deposit found on the bottom of the cell after the electrolysis of such a solution with an antimony cathode is ascribed to the same reaction. In the course of some earlier investigations (*Trans. Faraday Soc.*, in the press) fifteen of these deposits, produced under widely varying conditions, were examined. They included those produced (i) in the cathode compartment and on the cathode after electrolysis of (*a*) sodium hydroxide solutions (0·05—3*N*) with an antimony cathode, (*b*) solutions containing suspended metallic antimony or its compounds with a lead cathode, and (ii) by reduction of antimony compounds with nascent hydrogen. The anode was platinum and the current densities varied from 1 to 4 amps./cm.^{2}.

The deposits were filtered off, washed free from alkali, and dried as rapidly as possible by alcohol and ether, or by prolonged desiccation, and analysed by the measurement, using a Töpler pump, of the volume of hydrogen from 10 mg. liberated in a vacuum at a bright red heat. The amount of gas obtained varied from 0·01 to 0·25%, and was usually 0·1%. It burnt in a manner similar to hydrogen, but was not otherwise examined.

Since the compound Sb_2H_2 would contain 0·83% of hydrogen, it

seems probable that the deposits consisted of metallic antimony in a finely divided state, with small traces of adsorbed hydrogen which is removed only by the effect of heat at a low pressure. Further, the deposits resembled finely powdered pure metallic antimony both in appearance and in chemical properties, whereas those of antimony hydride behave quite differently (Weeks and Druce, *loc. cit.*). The deposits are produced by decomposition of the electrolytic stibine and not by cathodic disintegration, since they are obtained even with lead cathodes, and whereas the yield of stibine (calculated from the sum of that evolved as gas and that decomposed into metal and hydrogen) varies regularly with variations in the conditions of electrolysis, the relative proportions obtained in the form of gas or deposit are dependent only on the structure of the apparatus (Sand, Grant, and Lloyd, J., 1927, 378).—SIR JOHN CASS TECHNICAL INSTITUTE, LONDON, E.C.3. [*Received, May 16th,* 1928.]

NN′-Diphenyl-o-phenylenediamine. By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON.

FROM *o*-aminodiphenylamine and iodobenzene in boiling nitrobenzene solution, Wieland and Müller (*Ber.*, 1913, **46**, 3303) obtained a substance, m. p. 152·5°, which they described as *NN′*-diphenyl-*o*-phenylenediamine, $C_6H_4(NHPh)_2$. Clemo, Perkin, and Robinson (J., 1924, **125**, 1780 : errata, p. 2796) condensed 2′-aminodiphenylamine-6-carboxylic acid with *o*-chlorobenzoic acid and distilled the resulting 2′-*o*-carboxyphenylaminodiphenylamine-6-carboxylic acid; loss of carbon dioxide then took place and the product melted at 109°. They described this as *NN′*-diphenyl-*o*-phenylenediamine anc suggested that the compound obtained by Wieland and Müller wa not this substance but the isomeric *o*-aminotriphenylamine $NH_2{\cdot}C_6H_4{\cdot}NPh_2$. This suggestion is correct.

On carrying out the preparation described by Wieland and Mülle the product obtained had m. p. 149—150° and behaved like primary amine towards nitrous acid. The monoacetyl derivativ prepared by boiling this substance for 15 minutes with an excess acetyl chloride, had m. p. 131—132° after recrystallisation fro aqueous alcohol (Found: N, 9·4. Calc.: N, 9·3%). *o*-Amin triphenylamine was prepared by the method of Piccard and Brews (*J. Amer. Chem. Soc.*, 1921, **43**, 2630). This and the correspondi monoacetyl derivative proved to be identical with Wieland a Müller's supposed *NN′*-diphenyl-*o*-phenylenediamine and its mo acetyl derivative respectively. *o*-Nitrotriphenylamine (Piccard a Larsen, *J. Amer. Chem. Soc.*, 1917, **39**, 2006), crystallised fr ligroin (b. p. 60—80°), had m. p. 100°.

For the purposes of another investigation, we have prepared *NN'*-diphenyl-*o*-phenylenediamine in quantity by the method of Clemo, Perkin, and Robinson and through the kindness of these authors have been able to compare the final and intermediate compounds with original specimens.

In the condensation of *o*-aminodiphenylamine with iodobenzene it is therefore the secondary amino-group which is the more reactive, but in the condensation of 2'-aminodiphenylamine-6-carboxylic acid it is the primary amino-group which reacts. It is suggested that in the latter case the activity of the secondary amino-group is diminished or inhibited by internal salt formation with the adjacent carboxyl group.—GUY'S HOSPITAL MEDICAL SCHOOL (UNIVERSITY OF LONDON), S.E.1. [*Received, May 15th*, 1928.]

The Action of Disilicon Hexachloride on Ether. By FREDERIC STANLEY KIPPING and REGINALD AUBREY THOMPSON.

IT has been shown by Kipping and Murray (J., 1927, 2734) that ether reacts with silicon tetrachloride to a slight extent, giving some compound from which alcohol is produced on treatment with aqueous alkali. Disilicon hexachloride seems to behave in a similar manner.

A sample of the hexachloride (5—6 g.), carefully freed from titanium tetrachloride (this vol., p. 1377), was left in contact with about 10 volumes of ether. (The latter had been purified with sodium and by leaving it in contact with disilicon hexachloride during a week; it gave no reaction for alcohol.) Most of the ether was then distilled on the water-bath, excess of sodium hydroxide solution was added to the residue, and 4—5 c.c. of the aqueous solution distilled; the distillate gave with iodine and alkali a distinct precipitate of iodoform. The ether recovered from the first distillation was again mixed with the hexachloride, and the above operations repeated; iodoform was again obtained, and a further experiment with the same ether gave a like result. The quantity of iodoform produced in each experiment was only a few milligrams and was not appreciably increased by gently heating the mixture of the two substances: it seems, therefore, that the interaction is very limited, as in the case of silicon tetrachloride and ether.

It may be suggested that both the silicon chlorides form with ether additive products, corresponding with the compound $TiCl_4,Et_2O$ (Bedson, J., 1876, **29**, 311), and that these decompose at the ordinary temperature, or when they are gently heated, with formation of ethyl chloride and chloroethoxysilicon derivatives which are analogous to Bedson's titanium compound, $TiCl_3\cdot OEt$.

A sample of the silicon tetrachloride which had been used by Kipping and Murray in their experiments with ether was proved to have been free from titanium tetrachloride.—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, June 6th*, 1928.]

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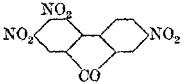
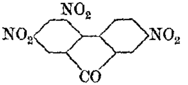
2 : 4 : 7-*Trinitrofluorenone*. By FRANK BELL.

THE interest attaching to heavily substituted fluorenones (Bell and Robinson, J., 1927, 1695) directed attention to the statement that fluorenone on nitration yields the 2 : 3 : 7-trinitro-derivative (I) (Schmidt and Bauer, *Ber.*, 1905, **38**, 3758). Apart from the exceptional orientation of this compound, its oxidation to yield 3 : 4-dinitrobenzoic acid called for further examination (for normal *method of oxidation of fluorenone derivatives, see Moore and Huntress, J. Amer. Chem. Soc.*, 1927, **49**, 1324).

(I.)   (II.)

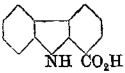
4-Nitrofluorenone, prepared from 4-nitrophenanthraquinone (Schmidt and Bauer, *ibid.*, p. 3741; Morgan and Thomason, J., 1926, 2695), was nitrated as follows: 1·25 g. in nitric acid (*d* 1·5; 25 c.c.) were warmed on a steam-bath for 2 hours, cooled, and poured into water. The precipitate after several crystallisations from benzene had m. p. 175° (Found: C, 49·5; H, 1·6. $C_{13}H_5O_7N_3$ requires C, 49·5; H, 1·6%). This trinitro-derivative must therefore be 2 : 4 : 7-*trinitrofluorenone* (II).

Fluorenone nitrated by the method of Schmidt and Bauer (*loc. cit.*) gave a product, m. p. 176° after repeated crystallisation from acetic acid or benzene (Found: C, 49·9; H, 1·8%). When mixed with the 2 : 4 : 7-trinitrofluorenone described above, it melted at the same temperature. Oxidation of this trinitro-derivative gave a very small amount of an impure acid, m. p. 165—170°. The m. p. of the purified acid would obviously exceed that of 3 : 4-dinitrobenzoic acid (164°).—BATTERSEA POLYTECHNIC, S.W.11. [*Received, June 8th*, 1928.]

Carbazole-1-carboxylic Acid. By EDWARD FULLER BRISCOE an SYDNEY GLENN PRESTON PLANT.

THE proof, hitherto lacking, that the acid obtained by the action (... dioxide on potassium carbazole at 270° (Ciamician and Silbe

Gazzetta, 1882, **12**, 272) or on magnesium 9-carbazyl iodide at 265—270° (Oddo, *ibid.*, 1911, **41**, i, 255) is carbazole-1-carboxylic acid, has now been furnished by boiling a mixture of tetrahydrocarbazole-8-carboxylic acid (Collar and Plant, J., 1926, 808) (12 g.), sulphur (3 g.), and pure quinoline (80 c.c.) under reflux for 12 hours and then pouring it on ice-dilute hydrochloric acid. The sticky product was dissolved in dilute aqueous sodium hydroxide, and the solution was boiled with charcoal, filtered, and acidified with hydrochloric acid. The crude acid was dried and then boiled for 6 hours with methyl-alcoholic hydrogen chloride. The methyl ester, obtained by pouring the solution into dilute ammonia, was distilled under reduced pressure, further purified by crystallisation from aqueous alcohol, and then hydrolysed with methyl-alcoholic sodium hydroxide. After recrystallising twice from toluene-petroleum, the resulting acid was obtained in yellowish plates, m. p. 268—269° (Found: C, 73·8; H, 4·5. Calc.: C, 73·9; H, 4·3%), which did not depress the m. p. (270—271°) of a specimen of carbazole-1-carboxylic acid prepared by the method of Ciamician and Silber.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, June 22nd*, 1928.]



CCLX.—*The Electrokinetic Potential between the Solid and Liquid States of a Single Substance.*

By FRED FAIRBROTHER and FRANK WORMWELL.

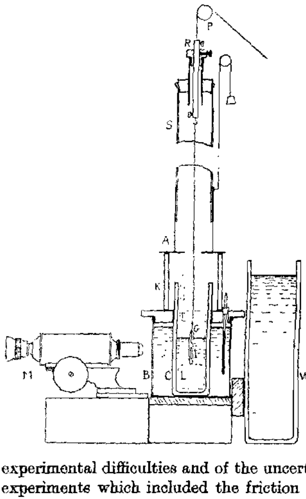
THE first observation of the production of an electric charge by the friction of a liquid against the same substance in the solid state appears to have been made in 1843 by Faraday ("Experimental Researches," **2**, No. 2131, p. 122), who, in the course of his researches on the production of electricity by escaping steam and air, allowed "undried common air" to issue under pressure from an orifice and flow along a cone of wood or metal which thereby became electrified, acquiring a negative charge. He showed that this electrification was due to the "particles of water suddenly condensed from the expanding and cooled air rubbing against the metal or wood" and that dry air produced no such electrification. When, however, undried air was let out against *ice*, it rendered the ice positive in contrast to the negative charge given to wood or metal.

Sohncke (*Wied. Ann.*, 1886, **28**, 550), on account of its bearing on the production of storm electricity, examined closely by different methods the electrification produced by the friction of water against ice. He allowed a jet of water from the ordinary tap to flow along

a plate covered with ice, and also forced water through a capillary formed along the axis of a rod of ice. By both methods he found the water to be negatively charged, thus confirming the results of Faraday.

The phenomenon seemed worthy of attention on account of its bearing on the structure of the interface between a solid and the melt from which it is crystallising or into which it is passing, as well as of its bearing on the general question of interfacial potentials. The sign of the electrokinetic potential of ice against water has therefore been examined by another method which has also permitted of the experiments being extended to other substances, with the result that, not only have the experiments of Faraday and Sohncke been confirmed, but in all cases where an electrokinetic potential was detected the solid was found to be positively charged relatively to the liquid.

FIG. 1.



EXPERIMENTAL.

Modifications of the stream potential method of Sohncke were tried but were discontinued on account both of the experimental difficulties and of the uncertainty of interpretation o: experiments which included the friction of the liquids against th electrodes. Electroendosmosis measurements were also attempte with little success. The chief difficulty here lay in the preparatio: of suitable capillaries or diaphragms, and in their retention for time sufficiently long to permit of the determination of the directio of electroendosmosis. The observations now recorded were ma by a cataphoresis method. In essentials the method is somewh similar to that used by Kleeman and Fredrickson (*Physical Rev.*, 192 **22**, 134) for the determination of the sign of the electrocapilla charge on thin metallic wires in water.

The apparatus employed is shown in Fig. 1. A rod or "icicle" I of the solid, formed round a thin glass rod G, was suspended at the end of a single unspun silk fibre, 141 cm. in length, in the corresponding liquid L. The glass rod was 3 cm. in length and 0·3 mm. in diameter. About three-quarters of the length of the rod of solid was immersed in the liquid, which was contained in the parallel-sided glass observation cell, C. This cell with its contents was surrounded by a water-jacket, B, with glass windows and a tightly fitting lid, whereby the liquid could be kept at a suitable temperature. With the present apparatus it was impracticable to keep the temperature at the triple point where solid, liquid, and vapour are in equilibrium. Temperatures slightly above or slightly below the melting point were therefore used, so that the rod of solid gradually melted away during the observations or gradually grew in size. This continual formation of a fresh interface also reduced the probability of erroneous observations conceivably due to the possible deposition of atmospheric moisture on the rod of solid during its formation. An electric field of 400 volts, giving about 50 or 100 volts per cm. according to the position of the electrodes, was applied through the electrodes, E, in a direction perpendicular to the plane of the paper. These electrodes in the preliminary experiments were of copper, but were later replaced by platinum electrodes, consisting of platinum foil stretched over rectangular frames of glass rod, and "soldered" in position by small globules of fusible lead glass. The suggestion that the observed effect might be due in part to the electrostatic attraction of such part of the suspended system as lay above the surface of the liquid but within the electric field, was carefully examined and eliminated by control experiments. The lateral movement of the rod of solid in the electric field was followed by means of the microscope, M, which was provided with an ocular micrometer. The suspended system was protected from draughts by the glass tube, S, over the lower end of which passed an earthed brass tube with a wide flange, A. The latter fitted on to the top of a light wooden box, K, formed on the top of the water-jacket lid. Slots were cut in the sides of this box to allow of the passage of the ends of the electrodes. A large glass cell W, filled with acidified ferrous sulphate solution, minimised the passage of heat from the lamp used for illumination. The rod of solid was formed as follows. A glass tube, about 4 cm. long, 2 mm. internal diameter, and closed at one end, was cleaned with chromic-sulphuric acid, washed with distilled water, and dried at 130° before each experiment. The tube was then filled with the liquid under investigation and arranged in the position later to be occupied by the rod of solid, and the glass rod

lowered into the liquid. For this purpose the observation cell with its contents and jacket was removed and the suspended system raised and lowered by a small winch operating a cord passing over a small pulley P. The weight necessary to the system was provided by a brass rod R working in a brass collar. The liquid was then allowed to solidify. For most purposes, in particular with substances melting below 30°, it was found advantageous to surround the small tube with dry, solid carbon dioxide. This quickened solidification and greatly facilitated the arrangement of the glass rod G in a central position in the "icicle." With substance melting above 30°, the final results were the same whether or no solid carbon dioxide was used. When the liquid was frozen, th glass tube was gently warmed with the fingers and the solid next t the glass melted sufficiently to allow the withdrawal of the remainin rod of solid. (In the case of substances melting above 30° th operation was usually carried out by immersing the tube in a sma quantity of the warm liquid.) The observation cell was the replaced, the rod of solid lowered into the liquid, and the cover placed in position. Usually about 15 seconds elapsed between t removal of the rod from the mould and its focussing in the field the microscope. By means of a reversing switch, observatio were taken with the electric field in both directions. Only obser ations which showed a definite reversal of direction of moveme with reversal of the applied potential were taken as indicative the electrokinetic charge. In all such cases the solid was positiv charged whether melting in a liquid a little warmer than itself growing in a supercooled liquid. In no case was a reversible mo ment observed in a direction indicating that the solid had a nega charge. On the other hand, in every case, except in benzene in *o*-chlorophenol, the (cleaned) glass rod alone in the liquid mo as if negatively charged, giving reversible deflexions usually gre than those of the rod of solid in the same liquid.

The width of the cell and the diameter of the rod of solid subst were such as to render negligible the effect of electroendosmosis a the walls of the observation cell. In any case this would ten produce an effect in a direction opposite to that actually obser

The choice of substances for examination was somewhat restri With the present form of apparatus it was inconvenient to use stances melting below 0° or above 40°. In the second place, it very desirable to use substances which formed coherent cryst rods. Several substances which were tried gave only soft, coherent masses or very viscous liquids. In all the observ now recorded, even with the rapid cooling employed, it co that the icicle was a compact *crystalline* mass, exc

the case of ice, which had the usual glassy form. The materials other than water were obtained initially in a fairly pure condition and were carefully fractionated after having been dried with the appropriate reagents, phosphoric oxide being used where permissible. No attempt, however, was made at intensive drying.

In the following table are given the substances examined, together with the typical deflexions from the mean position in terms of the divisions of the eyepiece micrometer, ten such divisions corresponding to an actual movement of 0·5 mm. In all cases, except with pure benzene and *o*-chlorophenol, for which no movement could be detected,* the sign of the charge on the solid was *positive*.

TABLE I.

Substance.	Dielectric constant.	M. p.	Electric field, volts/cm.	Typical deflexion.
Water	88·2 (0°) *	0°	50	10·0
Acetophenone	18·1 (21°) †	20	50	10·0
Nitrobenzene	37·5 (18°) ‡	5	50	2·0
Guaiacol	—	31	50	2·0
Anethole	—	21	100	2·0
p-Cresol	13 (40°) §	35	100	2·0
o-Cresol	8 (40°) §	31	100	1·0
o-Chloronitrobenzene	17·8 (33°) **	32	100	2·0
o-Chlorophenol	6·31 (25°) ‖	7	100	—
Benzene	2·28 (15°) ¶	5	100	—

* Drude, *Wied. Ann.*, 1896, **59**, 17.
† Walden, *Z. physikal. Chem.*, 1910, **70**, 569.
‡ Abegg and Seitz, *ibid.*, 1899, **29**, 242.
§ Philip and Haynes, J., 1905, **87**, 998.
‖ Sayce and Briscoe, J., 1926, 2623.
¶ Kerr, *ibid.*, p. 2796.
** Cauwood and Turner, J., 1915, **107**, 276.

The deflexion is greatest in the cases of water and acetophenone, and non-existent for *pure* benzene. It seems justifiable to conclude that it is only with "polar" compounds that the effect is observable, and that the more polar the substance is, the greater is the deflexion likely to be.

The movement in the case of acetophenone may seem surprisingly great compared with that of the other substances examined. The solid phase, however, owing to the manner of crystallisation when the rod was allowed to grow, had generally a very large surface compared with its weight. The positive charge on the solid acetophenone was also confirmed by the following observations. When slowly crystallising from a slightly super-cooled liquid, acetophenone forms large, very thin plates; when solidification was allowed to proceed in an electric field, it was clearly seen that more crystallisation occurred round the negative electrode than

* Another sample of benzene, which had not been completely freed from thiophen, gave indications of a positive charge on the solid state.

round the positive electrode. Also, plates of the solid lying in the surface of the liquid could occasionally be seen to move towards the negative electrode, reversing their movement when the direction of the applied potential was reversed.

In the case of *p*-cresol and o-chloronitrobenzene, too, small crystals in the interior of the liquid were seen to move towards the negative electrode.

The present data do not permit of any quantitative estimation of the charge on the solid, but an idea of the magnitude of the electrification may be gained from the fact that on the application of a field of 50 volts/cm., the small glass rod G alone, when suspended in distilled water, moved through 21 divisions of the eyepiece scale, having a negative charge. The electrification between the solid and liquid states of a substance is thus generally much less than the electrocapillary charge of glass in distilled water.

Discussion.

Some uncertainty exists regarding the change of dielectric constant on passing from the liquid to the solid state at the moment of solidification. There is considerable evidence from the results of several authors to show that at a temperature several degrees below the melting point, the dielectric constant of many solids is much less than that of the corresponding liquid, particularly when the latter is large, but that, as the melting point is approached, the dielectric constant of the solid becomes dependent to a greater extent upon the frequency of the measuring current, and may at low frequencies approach that of the liquid state. At the lower temperatures, the degree of freedom of the permanent dipoles in the solid is insufficient to permit of their contributing much to the dielectric constant.

If we regard the dielectric constant of the solid as being below that of the liquid during a change of state, then the observations now recorded are in contradiction to the rule formulated by Coehn (*Wied. Ann.*, 1898, **64**, 217), according to which the phase with the higher dielectric constant should become positively charged. Coehn (*loc. cit.*) realised this apparent anomaly in the case of ice and water, and suggested in explanation that probably it was not a matter of water rubbing against ice, but of water at a higher temperature rubbing against cooler water which was adhering to the ice. It seems very improbable, however, that the temperature coefficient of the dielectric constant of liquid water could account for such a degree of electrification as exists.

On the other hand, some recent work by Errera (*Trans. Faraday Soc.*, 1928, **24**, 162) indicates that in the neighbourhood of the melting point, the dielectric constant of a polar substance in the

solid state may, when measured at low frequencies, be even higher than in the liquid state. His figures for acetic acid show a sharp rise to a dielectric constant of 18 at a frequency of 680 cycles, in the neighbourhood of the solidification point, the dielectric constant of liquid acetic acid measured at the same frequency being about 6. Errera suggests in explanation of this rise that there is a formation at the moment of solidification of structures in a state of colloidal association, and he assumes further that "the arrangement of the molecular dipoles inside the colloidal structures is such that these last have a high electric moment, higher indeed than that of the molecular dipoles." If this phenomenon is general with polar substances, whatever its cause, then the sign of the electrification between the liquid and solid states of the same substance follows the general rule of contact electrification between different dielectrics as given by Coehn (*loc. cit.*).

It would appear, however, to be a general rule that, where there is an electrokinetic potential between the liquid and solid states, the solid is positively charged relative to the liquid.

We wish to acknowledge our indebtedness to the Chemical Society Research Fund and the Brunner-Mond Research Grant to this Department, which have partly defrayed the cost of this work. One of us (F. W.) also desires to thank the Department of Scientific and Industrial Research for a maintenance grant during its prosecution.

THE UNIVERSITY, MANCHESTER. [*Received, May 7th*, 1928.]

CCLXI.—*Studies of Valency. Part X. Electrometric Titration of Vernon's α- and β-Dimethyltelluronium Bases.*

By FRANK LATHE GILBERT and THOMAS MARTIN LOWRY.

IN a previous paper of this series (this vol., p. 307), it was shown that the isomeric bases from which the α- and β-dimethyltelluronium dihalides are derived are of the same order of strength as ammonia. The hydroxy-halides, on the other hand, although readily convertible into normal salts, are acid rather than basic in character, since they are approximately neutral towards indicators (such as methyl-orange and methyl-red) which give an end-point a little on the acid side of neutrality. This result can be interpreted most readily by saying that the kation of the hydroxy-halide $[TeMe_2OH]^+ Cl^-$ is more ready to lose a *hydrogen ion* according to

scheme 1, which leaves the octet intact, than to lose a second *hydroxyl ion*, as in scheme 2, in which the octet is converted into a sextet.

1. $[TeMe_2OH]^+ \rightleftharpoons [TeMe_2O] + H^+$;
compare $[NH_4]^+ \rightleftharpoons NH_3 + H^+$.
2. $[TeMe_2OH]^+ \rightleftharpoons [TeMe_2]^{++} + OH^-$.

An anomaly was encountered, however, in the fact that, whereas the molecular conductivities of the α-base varied from 1·9 to 3·4 ($v = 16$—256), those of the β-base varied only from 33 to 37 ($v = 32$—512), in spite of the much larger absolute values of the conductivities. By way of contrast, it may be recalled that the conductivity of diethylmercury hydroxide varies from 1·2 to 1·9 and that of hydrazine from 1·7 to 5·5, in the range $v = 16$—256, whilst the conductivity of methylamine varies from 21 to 70, that of dimethylamine from 24 to 81, and that of diethylamine from 31 to 93 in the same range. An electrometric investigation was therefore undertaken in order to compare the relative strengths of the two bases by the various electrical methods now available.

Conductivity of Bases.—Since the bases cannot be purified by crystallisation from solution, it was necessary to adopt other methods for checking their purity. The high conductivity of the β-base and the small increment on dilution might have been due to the presence of (i) undecomposed halide, (ii) silver compounds derived from the silver oxide used in the preparation of the bases, or (iii) trimethyltelluronium compounds formed by a molecular rearrangement of the β-base which is known to take place under the influence of alkalis. Since the β-base had been prepared by evaporating a solution of the α-base to dryness under reduced pressure, it was unlikely that its high conductivity could be due to undecomposed halide, for this must have been present also as an impurity in the α-base; and the presence, in solutions of the β-base, of dissolved silver compounds which were not also present in the α-base was even less probable, since they would be likely to be removed during the conversion of the α- into the β-base by evaporation. The possible presence of trimethyltelluronium salts was eliminated by preparing a solution of the β-base from the β-dibromide, in just the same way as the α-base was prepared from the α-salts.

The molecular conductivities of seven solutions of the two bases are in Table I. The values are rather less concordant than those of compounds which can be purified by ordinary methods; but the equivalent conductivities of the β-base were found to be consistently greater by about 30 units than those of the α-base, and to vary over the same small range on dilution. The most trustworthy values were obtained by preparing the β-base from a β-salt instead of

directly from the α-base, and their validity was confirmed by their close agreement with the conductivities of a sample which Vernon had obtained in a solid form by evaporating a solution of the base to dryness in a tube which was then sealed. The close concordance of these additional data shows that the results recorded in the previous paper were substantially correct, even although they may not be easy to explain.

TABLE I.

Molecular Conductivity ($\Lambda^{25°}$) *of Dimethyltelluronium Bases.*

		v = 16.	32.	64.	128.	256.	512.
α-Base :	Series 1	1·9	2·2	2·6	2·9	3·4	4·3†
	Series 2	3·2	3·5	3·8	4·1	4·8	6·3
	Series 3	2·7	3·1	3·5	3·9	4·8	6·0
β-Base.	From α-base : Series 1		34	35	36	37	37
	*Series 2		32	33	35	36	37
	From β-salt		30·7	31·9	33·3	34·5	35·6
	Vernon's sample		30·7	32·4	33·7	34·6	35·8

* This solution was evaporated *twice* to dryness, since a solution which had been evaporated only once gave conductivities about 2 units less than those recorded above.

† $\Lambda^{25°}$ = 6·0 at v = 1024.

Conductivity of Carbonates.—Since it appeared possible that some of the variations of conductivity might be due to the conversion of the bases into carbonates by absorption of atmospheric carbon dioxide, experiments were made to determine the magnitude of this effect, and the results are in Table II. The solutions of the

TABLE II.

Molecular Conductivity of Carbonates.

		v.	$\Lambda^{25°}$.
α-Base.	Original sample	32	3·22
	Saturated with CO_2 (40 mins.)	32	40·4
	Passed CO_2-free air (8 hours)	32	3·96
		64	4·2
		128	5·1
		256	6·8
		512	9·7
β-Base.	Original sample	32	31·0
	Passed CO_2-free air (4 hours)	32	31·6
	Saturated with CO_2 (40 mins.)	32	39·0
	Passed CO_2-free air (8 hours)	32	32·0

two bases were standardised by titration in the presence of bromophenol-blue. Since the molecular conductivity of a saturated solution of carbon dioxide ($M/30·3$) is $\Lambda^{25°} = 1·3$ (approx.), the molecular conductivities at $M/32$ would be increased by $1·3 \times 32/30·3 = 1·4$ on saturation with carbon dioxide, if no chemical combination occurred. In general, the conductivity of a base is

decreased by the presence of carbon dioxide, since the bicarbonate ion is much less mobile than the hydroxyl ion; but in the present instance the bases are so weak that this effect was reversed, and the conductivity was increased in each case to about 40 units. The carbonates are, however, so unstable, and their formation is so incomplete, that the maximum conductivity of the carbonated solutions was only about one-third of that of a typical binary electrolyte. Since, then, only about one-third of the base is present as carbonate, the carbon dioxide must also be held only reversibly; it was therefore removed completely by a current of purified air, the conductivities of the solutions falling again to values similar to those recorded in Table I.

$$TeMe_2(OH)_2 + CO_2 \underset{2}{\overset{1}{\rightleftharpoons}} [TeMe_2OH]^+ + HCO_3^-$$

It will be seen that the two bases are practically equal in their power of holding carbon dioxide. This result is not in agreement with the simple (but incorrect) deduction from the conductivities, that the β-base is perhaps 10 times stronger than the α-base; but it is in harmony with the results of the potentiometric titrations described below, which show that there is an intermediate stage of neutralisation within which the two bases are of nearly equal strength.

Conductivity Titrations.—In doing a conductivity titration it is usual to add a mineral acid to a solution of the base, and to observe the decrease of conductivity which takes place as the hydroxyl ions are replaced by chloride or bromide ions. In the case of the dimethyltelluronium bases this method cannot be used, since the conductivity undergoes only an insignificant increase as the feebly ionised base is converted into a more strongly ionised salt. A large decrease of conductivity was produced, however, when the α- or β-base was added to a mineral acid, since the mobile hydrogen ions of the acid were then replaced by the much more sluggish $[TeMe_2OH]^+$ ions of the hydroxy-salt.

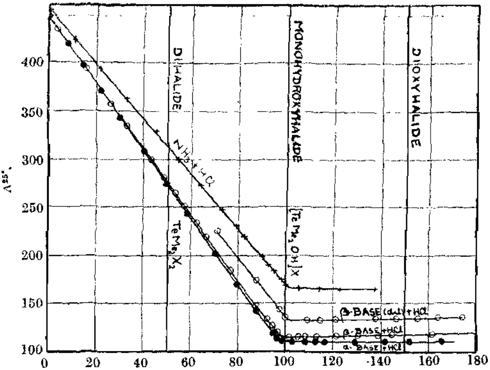
The titration curves are reproduced in Fig. 1, together with a curve for the neutralisation of *N*/10-hydrochloric acid by *N*/10-ammonia. The addition of the α-base (about *N*/7) to *N*/10-hydrochloric acid produced a continuous decrease of equivalent conductivity up to 100% neutralisation, after which the conductivity remained almost constant, since further additions of the weak α-base did not contribute substantially to the conductivity of the solution. The neutralisation curve shows a well-defined break, corresponding to the formation of the hydroxy-halide [α-$TeMe_2OH$]Cl; but no discontinuity at all can be seen at the composition $TeMe_2Cl_2$, which would be represented by the addition of *half* a molecular

proportion of the base to a molecule of the acid; and in the same way, no break was observed at points corresponding in composition to substances more basic than the hydroxy-halide.

The β-base (about $N/11$) gave a neutralisation curve of the same form as that of the α-base, with a well-defined break at the composition [β-$TeMe_2OH$]Cl, but no perceptible change of direction at the composition of the normal salt. In this case the specific conductivity was increased by adding an excess of the base, which has a substantial conductivity of its own; but no further discontinuity was observed in these more basic solutions. A duplicate determination with the β-base gave slightly higher molecular conductivities during neutralisation (perhaps because the acid was slightly stronger), but the remaining data agreed so closely with the earlier values that they could not be represented by a separate curve. On the other hand, a more dilute solution ($N/110$ approx.) gave higher equivalent conductivities throughout, the value at the neutral point being $\Lambda^{25^\circ} = 116$ (approx.) at $N/176$ as compared with 108 (approx.) at $N/29$.

FIG. 1.

Conductivity titrations.



Potentiometric Titrations with a Hydrogen Electrode.—α-Base. For these titrations, 20 c.c. of an $N/10$-solution of the α-base, which had been standardised by titration with methyl-orange as indicator,

were neutralised with 0·962*N*-hydrobromic or 0·198*N*-hydrochloric acid. The results were not very trustworthy, since the α-base poisoned the hydrogen electrode, giving rise to a progressive decrease of *E.M.F.* with time. An approximate result, obtained by passing a rapid stream of purified hydrogen over the electrode, showed, however, that equivalence was reached at the composition $TeMe_2(OH)Br$, and that there was no second inflexion at the point represented by $TeMe_2Br_2$.

β-*Base.* Similar experiments with the β-base gave two inflexions, one at 100%, corresponding to the formation of the hydroxy-halide [β-$TeMe_2OH$]Cl, and the other (much less sharply defined) at about 50% neutralisation, corresponding to the formation of a basic salt containing 2 mols. of the base to 1 mol. of acid. A white precipitate appeared in every case at about 75% neutralisation, reached a maximum, and then redissolved sharply at 100% neutralisation. A small quantity of the precipitate formed during the titration of the β-base with hydrobromic acid was collected, dried, and weighed. It was dissolved in water and acidified with nitric acid,* and silver nitrate added (0·0152 gram gave 0·0039 gram AgBr: Br = 10·9. $TeMe_2Br_2,7TeMe_2O$ requires Br, 10·5%). The precipitate, although collected from a nearly neutral solution, is therefore far more basic than the crystalline dioxy-iodide which Vernon prepared from the α-base.

Potentiometric Titrations with a Glass Electrode.—More trustworthy results were obtained by using a glass electrode of the type described by Hughes (this vol., p. 491), since this electrode is not poisoned by the tellurium bases. The electrode had been in constant use for some months and gave an *E.M.F.* of 55 millivolts per p_H, as compared with 58 millivolts for a hydrogen electrode. The titrations were made at atmospheric temperature (about 16°). The curves for six titrations are reproduced in Fig. 2.

α-*Base.* A solution of the α-base was standardised by titration with bromophenol-blue as indicator, since the approximate results obtained with the hydrogen electrode showed that the end-point of the titration would be given more correctly with this indicator than with methyl-orange. An *N*/10-solution (20 c.c.) was then titrated with *N*-hydrochloric acid. The potentiometric curve was confirmed by a duplicate determination in which the strength of the base was *N*/12·5. The foot of the curve was at 8·2 instead of 8·9; but the two curves then converged, and became coincident as the neutral point was approached.

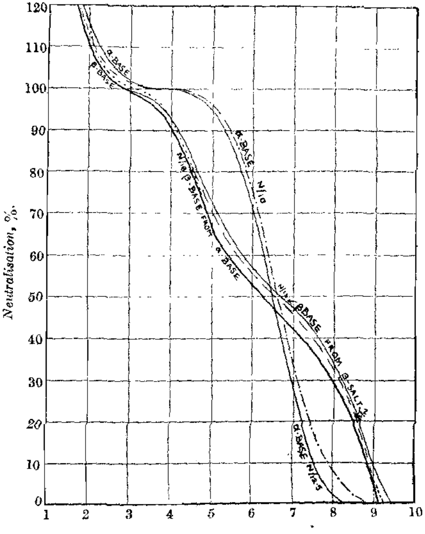
The curves have the characteristic form for a weak base, with

* No precipitate of dihalide was formed, such as always appears when acid is added to the α-hydroxy-salts.

a single inflexion at the composition of the hydroxy-halide [α-$TeMe_2OH$]Cl. The "equivalence point" is at $p_H = 3{\cdot}9$, and the inflexion is quite well defined, since $p_H = 4{\cdot}8$ at 98% and 3·0 at 102% neutralisation. Half-neutralisation occurs at $p_H = 6{\cdot}5$, from which it follows that $-\log K_b = 7{\cdot}5$. These results confirm the conclusion that $N/10$-solutions of the base can be titrated with

FIG. 2.

Potentiometric titrations.



nethyl-orange ($p_H = 2{\cdot}9$—$4{\cdot}0$), but would give a more trustworthy nd-point with bromophenol-blue ($p_H = 3{\cdot}0$—$4{\cdot}6$); for weaker olutions, a more acid indicator should be used.

β-*Base*. Four curves for the β-base are shown in Fig. 2. The ull curve is for an $N/16$-solution freshly prepared from the α-base, nd it agrees closely with the dotted curve for an $N/32$-solution of ernon's crystalline sample of the β-base (compare p. *1998*). Two

solutions, N/15·4 and N/21, prepared from the β-dibromide, were slightly more alkaline during the first half of the titration, but then the curves converged upon and became identical with the two curves for samples prepared from the α-base.

All the curves show an inflexion at the composition of the hydroxy-halide, [β-$TeMe_2OH$]Cl, together with a weaker inflexion at about 50% neutralisation; a white precipitate was also seen again between 75 and 100% neutralisation. The "equivalence point" is at $p_H = 3{\cdot}0$, but the inflexion is less well defined than in the case of the α-base, since $p_H = 3{\cdot}4$ at 98% and 2·6 at 102% neutralisation, giving a range of only 0·8 in place of 1·8 units; the end-point, even with the most suitable indicator (*e.g.*, methyl-orange), is therefore not likely to be very sharp.

The second inflexion, at 50% neutralisation, indicates that a basi(salt is formed in solution at a composition corresponding to th(formula $2TeMe_2O,HCl$; but, since the inflexion occurs at $p_H = 6{\cdot}5$ it follows that this basic salt is acid rather than alkaline in it reaction, and that (like the hydroxy-halide) it is therefore mor ready to part with a hydrogen than with a hydroxyl ion.

The formation of this basic salt makes it impossible to deduce th strength of the base in the usual way from the p_H at half-neutrali ation. Since, however, $p_H = 8{\cdot}3$ at 25% neutralisation, tl strength of the β-base may be deduced from the relation $-\log K_b$ · $\log (1 - x)/x + p_{K_w} - p_H$, where x is the degree of neutralisatio whence $-\log K_b = 6{\cdot}2$ for the free base. At 75% neutralisatic $p_H = 4{\cdot}8$ and $-\log K_b = 8{\cdot}7$ for the basic salt. The β-base therefore stronger than the α-base in the initial stages of neutral ation, but the basic salt which is then formed is not so strong the α-base; the weaker α-base thus gives a sharper end-point 100% neutralisation, and yields an α-hydroxy-halide which is m nearly neutral than the isomeric β-hydroxy-halide.

Hydrolysis of Basic and Normal Salts.—From the potentiom(curves it is possible to deduce a series of theoretical values for percentage hydrolysis of the hydroxy-salts as follows:

	$-\log K_b$.	K_b.	Hydrolysis a $v = 100$.	$v = 1$
[α-$TeMe_2OH$]Cl to free base ...	7·5	$3{\cdot}1 \times 10^{-8}$	0·6%	2%
[β-$TeMe_2OH$]Cl to basic salt ...	8·7	2×10^{-9}	2%	7%

The normal salts, on the other hand, are shown to be almost (pletely hydrolysed in water; but the percentage of unhydrol salt can be deduced from the fact that a saturated solution o α-di-iodide in cold water, which has a concentration of *N* shows an absorption band with a maximum extinction coeffi($\log \varepsilon = 2{\cdot}4$ at 3340 Å.U. Since a dry *alcoholic* solution o

di-iodide gives a maximum extinction coefficient, log ε = 3·7, at a slightly longer wave-length, we can (by ignoring the influence of the solvent) calculate that the *aqueous* solution contains only about 1/20 of its nominal content of iodide, or that the α-di-iodide is hydrolysed, to the extent of about 95%, to the hydroxy-iodide and hydriodic acid.

Basic Salts.—The potentiometric titrations of solutions of the β-base provide conclusive evidence of the formation of a basic salt, in which the acid and base are united in the ratio $2TeMe_2O,HCl$, to form (in Vernon's nomenclature) a "β-trioxychloride," since it could also be derived from three molecules of the base and one molecule of the normal salt. On the other hand, the potentiometric curves for the α-base agree with the conductivity titrations in giving no indications of the existence in solution of any salt but the hydroxy-halide. This result is remarkable in view of the fact that Vernon prepared from the α-base two basic salts which he formulated as follows:

(i) Di-iodotetramethylditelluronium oxide, $O(TeMe_2I)_2$.

(ii) Di-iodohexamethyltritelluronium dioxide, $TeMe_2(O{\cdot}TeMe_2I)_2$. The "*α-dioxyiodide*" (ii) *separates from water in large transparent* plates, with about $\frac{1}{2}H_2O$ of crystallisation; but it can also be obtained in anhydrous, colourless scales, *e.g.*, from concentrated ammonia, and can be prepared quite readily in this form by grinding the solid α-di-iodide with concentrated ammonia and then recrystallising it from aqueous ammonia. The "*α-monoxyiodide*" (i) separates as a bright yellow powder when an aqueous solution of the "dioxy-iodide" is boiled for some minutes and then cooled quickly.

Vernon states that the melting point of the monoxyiodide "fluctuates between 112° and 125°" and that "repeated analyses have shown considerable variations in both carbon and hydrogen." Our own experiments have shown that the yellow powder, which generally melts at about 116°, is stable if dried immediately; but, if it is allowed to stand in contact with water (or even in moist air) for some hours, it changes to a colourless form, which melts at 122°. Since it appeared likely that the pure *monoxyiodide* would be colourless like the dioxyiodide, we thought at first that the coloured form might be an aquo-compound, bnt this conclusion could not be confirmed by analysis. For instance, no difference could be detected between the halogen content of the yellow and the colourless form of the salt; and no change in weight was produced when a weighed quantity of the coloured powder was transformed to the colourless form by the action of water, and then dried. The conversion of the unstable into the stable form is therefore not accompanied by any important change of composition, and

may perhaps be formulated as depending on an interaction of the type $TeMe_2O + TeMe_2I_2 \rightleftharpoons I[TeMe_2{\cdot}O{\cdot}TeMe_2]I$, whereby a trace of coloured di-iodide is converted into a colourless oxyiodide. This change may perhaps be reversible in solution, but it proceeds to completion in one direction under the conditions of our experiments, and we have not yet been able to reproduce the yellow form from the stable colourless form by any direct process.

TABLE III.

Equivalent Conductivities of Basic Iodides at 25°.

	v = 128.	256.	512.	1024.	2048.
α-Monoxyiodide, $\frac{1}{2}(TeMe_2)_2OI_2$	94	98	100·5	102	105
α-Dioxyiodide, $\frac{1}{2}(TeMe_2)_3O_2I_2$	98	101	104	105	107

The equivalent conductivities of aqueous solutions of the monoxy iodide and dioxyiodide, reckoned in each case on the calculate concentration of iodine, are set out in Table III. The conductiviti differ only by a small amount, which corresponds roughly with t conductivity of the extra molecule of base in the latter compoun The values for the monoxyiodide are about six units lower th those recorded (this vol., p. 314) for solutions of the α-hydrox iodide made up by titration; but this discrepancy does not app to have any theoretical significance. The basic salts are inde disappointing compounds from the stoicheiometric point of vi and cannot be used with safety unless previously analysed. Th the yellow monoxyiodide is obviously a mixed product, and anhydrous form of the dioxyiodide is prepared by a method wh does not admit of any sharp separation from the less basic monc iodide. Finally, the crystalline form of the dioxyiodide cont "about half a molecule of water," which makes its chemical stitution difficult to interpret, and even throws doubt on the empi composition of any individual sample which has not been analy That these doubts are well founded is shown by the fact tha equimolecular mixture of the di-iodide with the dioxyiodide an *i*-factor of 2·2 in a freezing-point determination, and equiv conductivities ranging up to $\Lambda^{25°} = 140$ at $v = 2048$ litres; w we can only interpret on the supposition that the mixture w deficient in base that it was "extensively hydrolysed" in solu just as Vernon reported in the case of the monoxyiodide.

Freezing Points.—In addition to individual determinations freezing points of the α-monoxy- and dioxy-iodides, several ser measurements were made of the freezing points of solutions α- and β-bases during progressive neutralisation. In the

series, the bases were neutralised with hydriodic acid; but, as these measurements were complicated by the separation of precipitates, they were repeated with hydrochloric acid, and only the β-base then gave a transient white precipitate. The data are set out in Tables IV and V.

TABLE IV.

Freezing Points of Aqueous Solutions of α-Base.

(a) 14 c.c. of $N/9\cdot76$-α-base and N-HCl.

Neutralisation.	F. p.	*i*.
Water	= **2·969**	—
0%	2·756	1·11
13	2·750	1·16
25	2·757	1·15
38	2·750	1·21
51	2·748	1·25
60	2·735	1·34
67	2·729	**1·38**
76	2·718	1·47
86	2·704	1·56
95	2·683	1·70
101	2·671	**1·79**
108	2·660	1·87
124	2·630	2·09

(b) 14 c.c. of $N/9\cdot76$-α-base and N-HCl.

Neutralisation.	F. p.	*i*.
Water	= **2·966**	—
0%	2·752	1·12
13	2·752	1·15
25	2·749	1·18
35	2·747	1·21
44	2·739	1·27
54	2·733	1·32
60	2·728	1·36
67	2·721	**1·41**
76	2·711	1·49
86	2·707	1·53
95	2·691	1·64
101	2·679	**1·73**
108	2·665	1·83
130	2·628	2·12

(c) 15 c.c. of $N/10\cdot5$-α-base and $N/1\cdot05$-HI.

Neutralisation.	F. p.	*i*.
Water	= **3·057**	—
0%	2·845	1·20(?)
14	2·859	1·14
28	2·858	1·16
42	2·857	1·19
* 56	2·852	1·25
* 63	2·848	1·29
* 70	2·842	1·34
* 77	2·859	1·24
* 88	2·851	1·30
* 95	2·848	1·34
* 102	2·845	1·37
109	2·838	1·44
116	2·825	1·51
123	2·823	1·55
130	2·815	1·62
142	2·795	1·78
† 179	2·890	1·18

(d) 14 c.c. of $N/9\cdot76$-α-base and $N/1\cdot39$-HI.

Neutralisation.	F. p.	*i*.
Water	= **2·968**	—
0%	2·774	1·015
11	2·779	1·018
23	2·782	1·021
34	2·781	1·05
46	2·775	1·11
* 57	2·767	1·18
* 64	2·763	1·21
* 68	2·748	1·31
* 75	2·737	1·40
* 86	2·730	1·47
* 93	2·719	1·56
† 100	2·778	1·20
107	2·785	1·17
125	2·787	1·19

* A white precipitate appeared and disappeared between these limits.

† The separation of a permanent red precipitate of the di-iodide was followed by an abrupt rise of freezing point.

The freezing-point data confirm the conclusion that the free bases are dissociated only to a small extent in solution, the *i*-factor for both bases being about 1·1. On the other hand, the freezing points indicate that the hydroxy-halides are dissociated almost completely, the *i*-factor recorded for the α-hydroxy-chloride in two

TABLE V.

Freezing Points of Aqueous Solutions of β-Base.

(*a*) 15 c.c. of $N/15 \cdot 4$-β-base and N-HCl.

Neutralisation.	F. p.	*i*.
Water =	**2·966**	—
0%	2·836	1·10
18	2·827	1·18
36	2·813	1·31
54	2·800	1·44
72	2·781	1·62
* 87	2·770	1·73
* 96	2·759	1·83
105	2·748	1·95
128	2·727	2·15

(*b*) 15 c.c. of $N/15 \cdot 4$-β-base and N-HCl.

Neutralisation.	F. p.	*i*.
Water =	**2·966**	—
0%	2·829	1·14
14	2·822	1·20
27	2·822	1·22
41	2·815	1·29
50	2·810	1·33
59	2·804	1·39
68	2·800	1·44
* 77	2·789	1·54
* 91	2·783	1·61
* 100	2·769	1·74
114	2·744	1·98
132	2·707	2·32

(*c*) 15 c.c. of $N/15 \cdot 4$-β-base and $N/1 \cdot 39$-HI.

Neutralisation.	F. p.	*i*.
Water –	**3·023**	—
0%	2·887	1·13
15	2·882	1·18
30	2·878	1·23
44	2·879	1·24
59	2·875	1·29
67	2·874	1·31
74	2·867	1·38
† 85	2·870	1·36
† 93	2·873	1·35
100	2·880	1·29
108	2·865	1·43
122	2·869	1·41

* A white precipitate appeared and disappeared between these limits.

† A brownish-pink precipitate appeared and disappeared between these limits.

duplicate determinations being 1·79 and 1·73, whilst that for the β-hydroxy-chloride rose to 1·95 and 1·98 (corrected values, 1·90 and 1·84) in solutions from which a transient slight precipitate had been cleared by the addition of 5 and 14% excess of acid respectively. The *lower values recorded for the* α-*hydroxy-chloride may* be *due* to a partial formation, by loss of water, of a monoxy-chloride, which would give a maximum value $i = 1 \cdot 5$ (compare footnote, this vol., p. 319).

The freezing-point depressions for the iodide solutions are rendered uncertain by the separation of insoluble basic iodides; but the values of the *i*-factor, 1·34 and 1·31, for solutions corresponding in composition with Vernon's α-dioxyiodide, are in close agreement with three values, 1·38, 1·37, and 1·34, for more dilute solutions (0·024—0·006*N*) of the crystalline salt, although they are rather lower than the factors 1·55 and 1·57 calculated from two determinations of molecular weight by Vernon (J., 1921, **119**, 693). These values, which have been reckoned on the concentration of the base

in the solutions, are compatible with an almost complete dissociation of the α-dioxyiodide into α-hydroxy-iodide ($i = 1{\cdot}7$) and α-base ($i = 1{\cdot}1$), which would give an i-factor of 1·5.

Our own measurements of the freezing-point depression of a solution of the α-monoxyiodide lead to values, $M = 145$, $i = 2{\cdot}04$, which are in close agreement with the corresponding figures, $M = 143$, $i = 2{\cdot}07$, deduced from Vernon's measurements (J., 1921, **119**, 693); but, since they were made with the unstable yellow form, which is "extensively hydrolysed" by water (Vernon, *loc. cit.*), we do not regard them as trustworthy, and attach no importance to the fact that they are slightly in excess of the maximum theoretical value for complete hydrolysis of the oxyiodide, and complete ionisation of the resulting hydroxy-iodide. On the other hand, the i-factors for solutions prepared by adding hydriodic acid to the free base are too low, as a result of precipitation of insoluble products from the solution. The most trustworthy value, therefore, was obtained by dissolving the colourless oxyiodide (m. p. 122°) to a dilute solution, of concentration $0{\cdot}0254N$, which gave an i-factor 1·82, in good agreement with the values given by the soluble hydroxy-chlorides.

The i-factor for the β-base at 50% neutralisation is about 1·4 for each molecule of base, or 2·8 for a salt of the composition $2TeMe_2O,HCl$.

The following notes are made in reference to the products which separate from solution at different stages of neutralisation of the two bases by hydriodic acid.

α-*Base.* At 67% neutralisation (dioxyiodide) the solution first deposits the less soluble monoxyiodide, and then gives crystals of the hydrated dioxyiodide. The precipitate seen at about 80% neutralisation consists entirely of the monoxyiodide, but at 100% neutralisation the solution deposits both the monoxyiodide and the di-iodide.

β-*Base.* At 50% neutralisation (trioxyiodide) the solution slowly deposits a brown precipitate with no definite melting point; this precipitate is probably analogous to the basic bromide which is formed during the potentiometric titration of the β-base. At 67% neutralisation (dioxyiodide) the separation of the brown precipitate leaves a colourless solution from which the β-di-iodide is obtained. At 100% neutralisation, the normal product would be either a hydroxy-iodide, or a monoxyiodide formed from it by loss of water; actually, however, the solution deposits the β-di-iodide, leaving behind an alkaline solution of the base.

Summary.

(*a*) The molecular conductivity of the α-base at 25° varies fro 3 to 6, and that of the β-base from 31 to 36, in the range fro $v = 32$—512. The molecular conductivities are increased t about 40 (at $v = 32$) by saturation with carbon dioxide, but a reduced to normal values by passing a current of purified air throug the solutions.

(*b*) Conductivity titrations of the bases show a break at the com position of the hydroxy-halide, but give no indication of the presen in the solutions either of the normal salt or of any more basic com pound than the hydroxy-halide.

(*c*) Potentiometric titrations of the α-base with a glass electrod show the typical behaviour of a weak base, forming a nearly neutra hydroxy-salt; but they give no indication of the presence in solutio of the dioxyiodide which Vernon prepared in a crystalline form The curve for the β-base, on the other hand, shows an inflexion a about 50% neutralisation, corresponding with the formation of basic salt of the composition $2TeMe_2O,HCl$, which has not bee obtained in the free state.

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UNIVERSITY OF CAMBRIDGE. [*Received, May 31st*, 1928.]

CCLXII.—*Syntheses of Cyclic Compounds. Part III. The Reduction of Some Unsaturated Cyano-esters by Moist Aluminium Amalgam. A New Synthesis of Mono-substituted Malonic Acids and of ββββ′β′-Tetramethyladipic Acid. Further Evidence for the Multiplanar Configuration of the* cyclo*Heptane Ring.*

By ISRAEL VOGEL.

IN previous communications (J., 1927, 1985; this vol., p. 1013 it has been shown that whereas ethyl ethylidenemalonate (I) o reduction with moist aluminium amalgam yields almost exclusivel the bimolecular compound (II), ethyl benzylidenemalonate (III yields a mixture of the unimolecular compound (IV) and the bimolec- ular compound (V) in the proportion of approximately 2 to 1, a result which is obviously due to the presence of the phenyl group (compare Haerdi and Thorpe, J., 1925, **127**, 1237). It was clearly

desirable to study the corresponding *gem*-dimethyl, *cyclo*pentane, and *cyclo*hexane compounds in order to obtain some further inform-

(I.) $CHMe{:}C(CO_2Et)_2$ $\qquad$ $CHMe{\cdot}CH(CO_2Et)_2$ / $CHMe{\cdot}CH(CO_2Et)_2$ (II.)

(III.) $CHPh{:}C(CO_2Et)_2$ $\qquad$ $CHPh{\cdot}CH(CO_2Et)_2$ / $CHPh{\cdot}CH(CO_2Et)_2$ (V.)

(IV.) $CH_2Ph{\cdot}CH(CO_2Et)_2$

ation as to the effect of substituents. The *gem*-dimethyl compound, ethyl *isopropylidenemalonate* (VI), had already been prepared in poor yield by Meyenberg (*Ber.*, 1895, **28**, 785), but although an improved method for its preparation has been developed, this compound was not considered suitablo for investigation, since it could not be completely freed from ethyl malonate by simple means.

$CMe_2{:}C(CO_2Et)_2$ (VI.)

$CH_2{\cdot}CH_2$ / $CH_2{\cdot}CH_2$ $>C{:}C(CO_2Et)_2$ (VII.) $\qquad$ $CH_2<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{-}CH\end{matrix}>C{\cdot}CH(CO_2Et)_2$ (VIII.)

The *cyclo*pentane analogue (VII) is likewise difficult to prepare in a state of purity (Kon and Speight, J., 1926, 2727); and the *cyclo*hexane compound (VIII) normally possesses the βγ-structure (Kon and Speight, *loc. cit.*), rendering it valueless for the work in view. The unsaturated cyano-esters, however, were obtained in good yield and in a state of purity.

Ethyl *iso*propylidenecyanoacetate (IX) (Komppa, *Ber.*, 1900, **33**, 3530; Scheiber and Meisel, *Ber.*, 1915, **48**, 238; Birch and Kon, J., 1923, **123**, 2443) on reduction with moist aluminium amalgam in ether gave ethyl *r*-*iso*propylcyanoacetate (XI) (main product)

(IX.) $CMe_2{:}C(CN){\cdot}CO_2Et$ $\qquad$ $CMe_2{\cdot}CH(CN){\cdot}CO_2Et$ / $CMe_2{\cdot}CH(CN){\cdot}CO_2Et$ (X.)

(XI.) $CHMe_2{\cdot}CH(CN){\cdot}CO_2Et$

together with the bimolecular compound, *ethyl αδ-dicyano-ββγγ-tetramethylbutane-αδ-dicarboxylate* (X). The constitution of (XI) was established by hydrolysis with alcoholic potash to *iso*propylmalonic acid (Conrad and Bischoff, *Annalen*, 1880, **204**, 144; Stohmann, Kleber, and Langbein, *J. pr. Chem.*, 1889, **40**, 211), and that of (X) by conversion into the crystalline *amide* on treatment with concentrated ammonia and into ββ′β′-tetramethyladipic acid (Farmer and Kracovski, J., 1926, 2318; 1927, 681) by hydrolysis with concentrated hydrochloric acid. Condensation of ethyl *iso*propylidenecyanoacetate with alcoholic potassium cyanide (compare Lapworth and McRae, J., 1922, **121**, 2741) gave a 60% yield of *as*-dimethylsuccinic acid—this appears to be the best method of preparing this compound; Higson and Thorpe's process (J., 1906,

89, 1463) is less convenient and gives a smaller yield (40—45%; Farmer and Kracovski, *loc. cit.*).

The reduction of ethyl *cyclo*pentylidenecyanoacetate (XII) (Harding and Haworth, J., 1910, **97**, 486) with moist aluminium

$$\begin{matrix}CH_2\cdot CH_2 \\ CH_2\cdot CH_2\end{matrix}\!\!>C{:}C(CN)\cdot CO_2Et \quad \text{(XII.)} \qquad \begin{matrix}CH_2\cdot CH_2 \\ CH_2\cdot CH_2\end{matrix}\!\!>CH\cdot CH(CN)\cdot CO_2Et \quad \text{(XIII.)}$$

$$\text{(XIV.)} \quad \begin{matrix}C_4H_8>C\cdot CH(CN)\cdot CO_2Et \\ C_4H_8>C\cdot CH(CN)\cdot CO_2Et\end{matrix} \qquad \begin{matrix}C_4H_8>C\cdot CO_2H \\ CH_2\cdot CO_2H\end{matrix} \quad \text{(XV.)}$$

amalgam gave *ethyl* r-cyclo*pentylcyanoacetate* (XIII) (which on hydrolysis with alcoholic potassium hydroxide yielded cyclo*pentylmalonic acid*) and a small quantity of a high-boiling bimolecular compound (XIV). Condensation of (XII) with alcoholic potassium cyanide gave a good yield of 1-carboxy*cyclo*pentane-1-acetic acid (XV), a compound first prepared in small quantity by Norris and Thorpe (J., 1921, **119**, 1208) by the oxidation of *cyclo*pentane-*spirocyclo*hexane-3 : 5-dione. The *anhydride* of this substituted succinic acid is only relatively slowly affected by water, concentrated hydrochloric acid, and by alkalis in the cold but is converted into the acid on boiling for a short time.

In a similar manner the main product of the reduction of ethyl *cyclo*hexylidenecyanoacetate (Harding, Haworth, and Perkin, J., 1908, **93**, 1943) (XVI) with moist aluminium amalgam was *ethyl* r-cyclo*hexylcyanoacetate* (XVII), characterised by conversion into *cyclo*hexylmalonic acid on hydrolysis with alcoholic potassium hydroxide; a small quantity of the dicyano-ester (XVIII) was also produced. 1-Carboxy*cyclo*hexane-1-acetic acid is obtained in good

$$\text{(XVI.)} \quad CH_2\!<\!\begin{matrix}CH_2\cdot CH_2 \\ CH_2\cdot CH_2\end{matrix}\!>C{:}\overset{CO_2Et}{C}\cdot CN \qquad CH_2\!<\!\begin{matrix}CH_2\cdot CH_2 \\ CH_2\cdot CH_2\end{matrix}\!>CH\cdot\overset{CO_2Et}{CH}\cdot CN \quad \text{(XVII.)}$$

$$\text{(XVIII.)} \quad \begin{matrix}C_5H_{10}>C\cdot CH(CN)\cdot CO_2Et \\ C_5H_{10}>C\cdot CH(CN)\cdot CO_2Et\end{matrix} \qquad \begin{matrix}C_5H_{10}>C\cdot CO_2H \\ CH_2\cdot CO_2H\end{matrix} \quad \text{(XIX.)}$$

yield by the interaction of the unsaturated cyano-ester (XVI) and alcoholic potassium cyanide (Lapworth and McRae, J., 1922, **121**, 2741; compare Norris and Thorpe, J., 1921, **119**, 1209), and its anhydride has the remarkable property of being only slowly affected by water, aqueous sodium carbonate and by hydrochloric acid even on boiling. The anhydrides of these "cyclic" *succinic acids appear to be intermediate in chemical properties between ordinary unsubstituted anhydrides and those of tetraethyl- and tetrapropylsuccinic acids* (Walker and Walker, J., 1905, **87**, 961; Crichton, J., 1906, **89**, 929), which are derived almost *spontaneously from the*

acids—an experimental fact in striking agreement with the Thorpe–Ingold theory. It is hoped to make a quantitative study of the ease of fission and of formation of these substituted anhydrides in the near future.

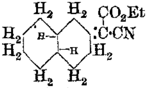
Suberone reacts with ethyl cyanoacetate in the presence of piperidine with the formation of *ethyl* cyclo*heptylidenecyanoacetate* (XX);

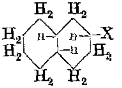
$$\text{(XX.)}\quad \begin{matrix} CH_2\cdot CH_2\cdot CH_2 \\ CH_2\cdot CH_2\cdot CH_2 \end{matrix}\!\!>C{:}C(CO_2Et)\cdot CN \qquad \begin{matrix} CH_2\cdot CH_2\cdot CH_2 \\ CH_2\cdot CH_2\cdot CH_2 \end{matrix}\!\!>CH\cdot CH(CO_2Et)\cdot CN \quad \text{(XXI.)}$$

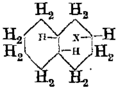
$$\text{(XXII.)}\quad \begin{matrix} C_6H_{12}>C\cdot CH(CN)\cdot CO_2Et \\ C_6H_{12}>C\cdot CH(CN)\cdot CO_2Et \end{matrix} \qquad \begin{matrix} C_6H_{12}>C\cdot CO_2H \\ CH_2\cdot CO_2H \end{matrix} \quad \text{(XXIII.)}$$

the yield, however, is less than those of the corresponding *gem*-dimethyl, *cyclo*pentane and *cyclo*hexane compounds. Reduction of (XX) with moist aluminium amalgam yielded *ethyl* r-cyclo*heptylcyanoacetate* (XXI) (characterised by the formation of cyclo*heptylmalonic acid* on hydrolysis with alcoholic potash) and the *dicyano-ester* (XXII). The bimolecular compound (XXII) is produced in better yield than the corresponding *cyclo*hexane compound; the significance of this fact is discussed later (p. 2015). The condensation of ethyl *cyclo*heptylidenecyanoacetate with alcoholic potassium cyanide resulted in a good yield of 1-carboxy*cyclo*heptane-1-acetic acid (XXIII), a compound first prepared in minute amount by Dickens, Horton, and Thorpe (J., 1924, **125**, 1840) by the interaction of *cyclo*heptanonecyanohydrin and ethyl sodiocyanoacetate and subsequent hydrolysis. The *anhydride* resembles the *cyclo*hexane analogue in properties.

trans-β-Decalone (Hückel, *Annalen*, 1925, **441**, 1) condenses more readily than suberone with ethyl cyanoacetate in the presence of piperidine, yielding *ethyl* trans-*decahydro*-β-*naphthylidenecyanoacetate* (XXIV), which on reduction with moist aluminium amalgam gave only one r-trans-*decahydro*-β-*naphthylcyanoacetate* (XXV or XXVI), and only one *decahydro*-β-*naphthylmalonic acid*


(XXIV.)


(XXV.)


(XXVI.)

$X = CH(CN)\cdot CO_2Et$

[$X = CH(CO_2H)_2$] was produced on hydrolysis of the latter with alcoholic potassium hydroxide. A careful search did not reveal the presence of the second theoretically possible saturated cyano-ester or malonic acid (compare Perkin and Sedgwick, J., 1924, **125**,

2437; 1925, **127**, 439, who were able to isolate only one octahydroacridine by the reduction of tetrahydroacridone with sodium amalgam).

The results are in harmony with the complete mechanism of the aluminium amalgam reduction process (this vol., p. 1017). The poor yields of the bimolecular compounds must be attributed to the presence in $CR_1R_2{:}C(CN){\cdot}CO_2Et$ of groups R_1R_2 of relatively large molecular volume —" the volume factor "—and also to the presence of the strongly negative cyano- and carbethoxyl groups—" the polar factor "—both of which will tend to render the formation of bimolecular layers difficult. Since the second effect is constant throughout the series, one has here a possible method of determining the configuration of simple rings. The *cyclo*pentane ring is usually regarded as having the relatively strainless uniplanar configuration, and the work of Thorpe and Ingold and their collaborators on *spiro*-compounds (J., 1915—1926), of Thorpe and others on ring-chain tautomerism (J., 1922 *et seq.*), and numerous incidental observations make it extremely probable that the *cyclo*hexane ring is relatively strained and has a uniplanar structure. On this basis, *i.e.*, assuming the uniplanar configurations of these rings, the angle θ (*vide infra*) has been computed by Thorpe and Ingold. It is suggested that the yields of bimolecular products are probably dependent on the tetrahedral angle θ, *i.e.*, on the strain in the ring. If this were so and the *cyclo*heptane ring had a uniplanar configuration, one would anticipate a progressive decrease in the yields of the bimolecular compounds on reduction of the appropriate unsaturated cyano-esters under comparable conditions. If, on the other hand, the strain in the *cyclo*heptane ring is relieved by its having a multiplanar structure, an increased yield of the bimolecular compound would be anticipated in the *cyclo*heptane series. The experimental results are exhibited in Table I and it will be seen that in every case more

TABLE I.

(A) $CHR_1R_2{\cdot}CH(CN){\cdot}CO_2Et$

$$\begin{matrix} CR_1R_2{\cdot}CH(CN){\cdot}CO_2Et \\ | \\ CR_1R_2{\cdot}CH(CN){\cdot}CO_2Et \end{matrix} \quad (B)$$

$CR_1R_2{:}C(CN){\cdot}CO_2Et$.	$\begin{matrix}R_1\\R_2\end{matrix}{>}C{<}\theta$.	Yield % (A).	Yield % (B).
R_1R_2 = *gem*-dimethyl	109·5°	63	21
CR_1R_2 = *cyclo*pentane	109·3	79	13
CR_1R_2 = *cyclo*hexane	107·2	84	6
CR_1R_2 = *cyclo*heptane	105·3	72	12

than 80% of the initial material has been accounted for and that there is no doubt that the yield of the bimolecular compound is much greater in the *cyclo*heptane than in the *cyclo*hexane series.

'his, then, would appear to provide evidence for the multiplanar onfiguration of the seven-membered ring, a result in accord with he conclusions reached by other workers (compare Baker and ngold, J., 1923, **123**, 122; Dickens, Horton, and Thorpe, J., 1924, **25**, 1830; Baker, J., 1925, **127**, 1678; Meerwein, *J. pr. Chem.*, 922, **104**, 161). Physico-chemical evidence in support of this view provided by measurements of the parachor (*vide infra*, p. 2018).

A few preliminary experiments, for which no great accuracy is laimed, were made on the effect of substituent groups on the rate f esterification in the succinic acid series. The yields of the iethyl esters under fairly comparable conditions for succinic acid, s-dimethylsuccinic acid and 1-carboxy*cyclo*pentane-1-acetic acid ere respectively 74%, 65% and 62%; these are in agreement with hat would be anticipated from the angles 115·3°, 109·5° and 109·3° alculated on the Thorpe–Ingold theory of valency deflexion. The esults of a detailed investigation, comprising all the substituted uccinic acids described in this paper, on the rates of hydrolysis and f esterification will form the subject of a future communication.

Various physical constants of some esters have been determined r calculated (see Tables II and III). The refractive indices are r the D line at about 20°; the exact temperatures are given in e experimental section. The surface tensions and densities were etermined over a range of temperatures and have been reduced to)°, a linear variation with temperature being assumed. The arachors [*P*] (obs.) are computed from the formula $P = \gamma^{\frac{1}{4}} M/d$, here M is the molecular weight, γ is the surface tension, and d is e density at the same temperature. For the calculated values the parachor, $\Sigma[P]$ (calc.), the structural and the atomic constants Sugden (J., 1924, **125**, 1187 and subsequent papers) have been nployed. The constants for the *cyclo*heptane * and decahydro-naphthalene rings have been taken as 3·6 and 12·2 respectively *ide infra*). It will be seen (Table II) that there is a regular crease in the boiling point, refractive index, and surface tension the size of the substituent ring is increased. The agreement tween the observed and the calculated values of the parachor for e cyclic compounds is satisfactory; ethyl *r-iso*propylcyanoacetate hibits an anomaly of − 5·0 which is due to the presence of the *m*-dimethyl group. This negative anomaly in compounds con-ining *gem*-dimethyl groups has been previously observed by Sugden d Wilkins (J., 1927, 139) for ethyl caronate and by Sugden is vol., p. 410) for certain phorone derivatives, but no explanation s yet been advanced.

* *A provisional value deduced from the parachors of ethyl cyclo*heptyl-*noacetate and suberone.*

TABLE II.

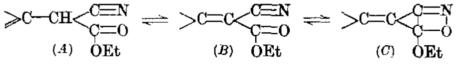
Cyano-esters $CHR(CN)\cdot CO_2Et$.

R —	*iso*-Propyl.	*cyclo*-Pentyl.	*cyclo*-Hexyl.	*cyclo*-Heptyl.	Decahydro-β-naphthyl.
B. p. (mm.) ...	99°/16	129°/13	145°/14	149°/11	186°/12
n_D	1·4243	1·4536	1·4612	1·4664	1·4802
$d_{4^\circ}^{20^\circ}$	0·9855	1·0246	1·0210	1·0206	1·0301
$[R_L]_D$ (obs.) ...	40·08	47·86	52·39	56·78	68·73
$[R_L]_D$ (calc.) ...	39·62	47·65	52·21	56·89	68·54
γ_{20°	31·82	34·77	35·58	36·09	36·33
$[P]$ (obs.)	374·8	430·1	467·6	502·7	594·6
$\Sigma[P]$ (calc.) ...	379·8	431·6	468·7	505·2	596·6

TABLE III.

	(XVI.)	(XX.)	(XXIV.)	(III.)	(IV.)
B. p. (mm.) ...	151°/12	160°/12	196°/14	179·5°/14	163°/14
n_D	1·4974	1·5003	1·5108	1·5380	1·4872
$d_{4^\circ}^{20^\circ}$	1·0558	1·0536	1·0519	1·1037	1·0759
$[R_L]_D$ (obs.) ...	53·57	57·86	70·34	70·25	66·95
$[R_L]_D$ (calc.) ...	51·80	56·62	68·08	—	—
γ_{20°	37·89	37·57	37·51	38·68	35·59
$[P]$ (obs.)	454·7	487·7	582·3	561·1	567·7
$\Sigma[P]$ (calc.) ...	457·7	494·2	585·6	559·7	570·7

The exaltations of molecular refractivity of the unsaturated compounds (Table III) are due to the presence of conjugated double bonds. The observed and the calculated values of the parachor agree to within 1% except for ethyl *cyclo*heptylidenecyanoacetate (XX), where the difference is slightly greater. The low values for the unsaturated cyano-esters may be due to the fact that these compounds may exhibit, in addition to ordinary three-carbon tautomerism ($A \rightleftharpoons B$), ring-chain valency tautomerism ($B \rightleftharpoons C$) to a very small degree (compare Ingold and Shoppee, this vol., p. 365; Sugden, *ibid.*, p. 410). No chemical evidence has yet been obtained in support of this suggestion.



(*A*) (*B*) (*C*)

The results for the homologous ketones *cyclo*pentanone (D), *cyclo*hexanone (E), and *cyclo*heptanone (F) and for *trans*-β-decalone (G), regenerated from their crystalline bisulphite compounds, are in Table IV. The refractive index and the surface tension both increase as the series is ascended. The line headed $\Sigma[P]$ (calc.) comprises the sum of the atomic constants plus the value for one double bond, and $[P]$ (obs.) — $\Sigma[P]$ (calc.) therefore gives the value of the ring constant determined experimentally. The calculated values of the ring constant have been computed from the " degree of unsatur-

TABLE IV.

	D.	E.	F.	G.
B. p. (mm.)	129·5°/761·5	47°/15	71°/19	106°/12
n_D	1·4383	1·4521	1·4635	1·4809
$d_{4°}^{20°}$	0·9486	0·9457	0·9496	0·9787
$[R_L]_D$ (obs.)	23·18	27·89	32·44	44·44
$[R_L]_D$ (calc.)	23·10	27·72	32·34	43·99
$\gamma_{20°}$	33·85	34·51	35·37	36·57
$[P]$ (obs.)	214·2	251·4	288·0	382·4
$\Sigma[P]$ (calc.)	204·0	243·0	282·0	364·8
Ring constant (obs.)	10·2	8·4	6·0	17·6
Ring constant (calc.)	9·3	7·7	6·6	15·4

ation " (Sugden and Wilkins, J., 1927, 142), and that for decahydronaphthalene is assumed to be the sum of the values for two *cyclo*hexane rings. The agreement between the observed and the calculated values of the ring constant is noteworthy, but the " constants " vary slightly from substance to substance, being influenced by substitution (compare Sugden and Wilkins, *loc. cit.*). The constants employed in computing $\Sigma[P]$ (calc.) in Tables III and IV are the mean *experimental* values of Sugden (J., 1924, **125**, 1185).

The constant obtained for the *trans*-decahydro-β-naphthalene ring (17·6) is practically twice that found for the *cyclo*hexane ring (8·4); this supports the view that the two rings from which the *trans*-decahydro-β-naphthalene molecule is built up are structurally similar (compare *Ann. Rep.*, 1927, **24**, 99). The ring constants for quinoline (Morgan and Thomssen, *J. Amer. Chem. Soc.*, 1911, **33**, 657; Sugden, J., 1924, **125**, 1187) and naphthalene (Bhatnagar and Singh, *J. Chim. phys.*, 1928, **25**, 21) are respectively 15·0 and 11·7, thus indicating that the structural constant in both cases is that for two six-membered rings.

Almost the only evidence which has been adduced in favour of the multiplanar configuration of large-membered rings (from seven upwards) is that based on the determination of the molecular volume (molecular weight/density) (Ruzicka, Brugger, Pfeiffer, Schinz, and Stoll, *Helv. Chim. Acta*, 1926, **9**, 499). The work of Sugden and his collaborators has shown that much more trustworthy values are obtained by comparing molecular volumes at temperatures at which the substances have the same surface tension, or, in other words, by the measurement of the parachor. Theoretically, it would be expected that the difference in the magnitude of the parachor for CH_2 in large rings would approximate to 39·0, the value for CH_2 in an open-chain system, if the large rings are multiplanar and therefore largely collapsed, so that the effect of an additional CH_2 group would be almost the same as its effect in a similarly crumpled aliphatic chain (compare *Ann. Rep.*, 1926, **23**, 117). No trustworthy surface tension data are available for cyclic hydrocarbons. The

parachors, however, can be readily calculated from the observed values for the cyclic ketones by substituting the value of 2H for :O, both of which are known with some accuracy; the results are under $[P]_1$ in Table V.

TABLE V.

	5-Ring.	6-Ring.	7-Ring.......	15-Ring.	16-Ring.
$[P_1]$	205·2	242·4	279·0	—	—
$[P_1]/n$	41·0	40·4	39·7	—	—
$\Sigma[P]$ (calc.)...........	204·3	241·7	279·6.........	588·1	626·9
$\Sigma[P]/n$ (calc.)	40·9	40·3	39·9.........	39·2	39·2

$[P_1]/n$, where n is the number of CH_2 groups in the cyclic hydrocarbon, represents the observed volume occupied by the CH_2 group plus a share of the internal space of the ring. The value for CH_2 in the *cyclo*heptane ring approximates closely to that for CH_2 in an open-chain hydrocarbon and thus gives further support to the view that the seven-membered ring is multiplanar (p. 2015). According to Mohr (*J. pr. Chem.*, 1922, **103**, 316) there are two "strainless" forms of the *cyclo*heptane ring, each of which occupies three planes.

Since, however, the isomerism demanded by these forms has not yet been observed experimentally, it must be assumed that these merely represent phases of the contortions of the molecule.

The parachors of the cyclic hydrocarbons have been computed from the sum of the atomic constants plus the ring constant, the latter being derived from the "degree of unsaturation" (Sugden and Wilkins, J., 1927, 142), and are given in the line $\Sigma[P]$ (calc.); the contribution per CH_2 group is given in the last line of the table. The agreement between experiment and theory for the 5-, 6-, and 7-membered rings is satisfactory and it is hoped to extend the results to larger rings as soon as the necessary materials have been obtained.

The work is being continued and will include a study of the alkylation of the saturated cyano-esters and the optical resolution of the corresponding cyano-acids and their derivatives.

EXPERIMENTAL.

Ethyl isoPropylidenemalonate (VI).—Ethyl malonate (100 g.), acetone (54 g., dried over calcium chloride), acetic anhydride (80 g.),

and zinc chloride (23 g.) were heated in a closed vessel at 100° for 36 hours. The products of three such condensations were freed from most of the acetic anhydride and acetic acid by distillation (up to 140°); from the residue, a fraction distilling above 90°/20 mm. was collected, the distillation being stopped when the pressure had risen to 50 mm. On refractionation, ethyl malonate (40 g.) distilled at 90—110°/20 mm. and ethyl *iso*propylidenemalonate (195 g.) at 110—128°/20 mm. For use in syntheses, the latter was redistilled and the middle fraction collected.

Attempts to synthesise norpinic acid by the condensation of ethyl *iso*propylidenemalonate with ethyl sodiocyanoacetate, followed by treatment with methylene iodide and subsequent hydrolysis, under a large variety of conditions were all unsuccessful owing to the tendency of the initial Michael addition product to lose ethyl malonate.

gem-*Dimethyl Series.*

Ethyl α-Cyano-ββ-dimethylacrylate (IX).—A mixture of 200 g. of dry acetone and 200 g. of ethyl cyanoacetate was treated with 2 g. of piperidine. The deep yellow solution obtained was kept for 60 hours, refluxed for 4 hours, and again kept for 60 hours. Ether was then added and the solution was washed with dilute hydrochloric acid and with water, dried with anhydrous sodium sulphate, and distilled. The pure compound distilled at 114—116°/14 mm. (mainly at 115°/14 mm.) and, unless precautions were taken, solidified in the condenser. Yield, 147 g. or 54%. It had m. p. 33° after being spread on a porous tile (Komppa, *loc. cit.*, gives m. p. 28°; Birch and Kon, *loc. cit.*, p. 2447, give b. p. 117—127°/20 mm. and state that it "solidifies when cooled in ice.").

Reduction with Moist Aluminium Amalgam in Ether. Preparation of Ethyl r-iso*Propylcyanoacetate* (XI) *and of Ethyl αδ-Dicyano-ββγγ-tetramethylbutane-αδ-dicarboxylate* (X).—The ester (50 g.) was reduced with 75 g. of moist aluminium amalgam (J., 1927, 594), and the product worked up after 7 hours. On distillation, ethyl *iso*propylcyanoacetate (31·5 g.) passed over at 100—101°/15 mm., leaving a high-boiling residue (10·5 g.). The former on refractionation distilled at 99°/16 mm. (Fischer and Flatau, *Ber.*, 1909, **42**, 2983, give b. p. 115—116°/24—25 mm.) and had $n_D^{17·2°}$ 1·4243, $d_4^{17·2°}$ 0·9880, $[R_L]_D$ 40·08 (calc., 39·62) (Found: C, 61·8; H, 8·3. Calc.: C, 61·9; H, 8·4%). The latter, an extremely viscid reddish-brown oil, was treated for 48 hours with a large excess of ammonia (*d* 0·88); the product, after being washed with dilute hydrochloric acid, was crystallised twice from dilute methyl alcohol, the *monoamide* of (X) separating in small, thin prisms, m. p. 95° (Found: C, 60·5; H, 7·7;

M, in camphor by Rast's method, 275. $C_{14}H_{21}O_8N_3$ requires C, 60·2; H, 7·6%; *M*, 279).

Hydrolysis of the Ester (X). *Preparation of* ββ β'β'-*Tetramethyladipic Acid*.—The high-boiling product was boiled for 5 hours with concentrated hydrochloric acid (10 parts); after 12 hours, ββ β'β'-tetramethyladipic acid, accompanied by a very small quantity of carbonaceous matter, separated. The acid crystallised from hot water in colourless thin prisms, m. p. 207° alone or mixed with an authentic specimen (Farmer and Kracovski, J., 1926, 2322). This appears to be the most convenient mode of preparing this acid.

Hydrolysis of the Ester (XI). *Preparation of* iso*Propylmalonic Acid*.—Solutions of the ester (18 g.) in rectified spirit (36 g.) and of potassium hydroxide (31 g.) in water (62 g.) were mixed, refluxed for 14 hours, and evaporated to dryness. An aqueous solution of the residue was shaken with ether to remove any unchanged ester, if present, acidified with dilute sulphuric acid, and extracted five times with ether; from the extract, *iso*propylmalonic acid was obtained as an oil which crystallised completely when left over concentrated sulphuric acid in a vacuum desiccator (yield, 12·6 g. or 75%). The acid crystallised from hot chloroform in prisms containing chloroform of crystallisation which was lost on exposure to air; the opaque white residue had m. p. 87—88° after 24 hours, m. p. 88—89° (decomp.) after 48 hours, and was then unaffected by further exposure to the atmosphere (Found: C, 49·2; H, 6·9; equiv., by titration, 74. Calc.: C, 49·3; H, 6·9%; equiv., 73). Similar behaviour was observed by Romburgh (*Rec. trav. chim.*, 1886, **5**, 238), who found that the acid crystallised from benzene with 2 molecules of benzene of crystallisation which were lost on exposure to the atmosphere; the residue melted at 87°.

Condensation of the Ester (IX) *with Alcoholic Potassium Cyanide. Preparation of* as-*Dimethylsuccinic Acid*.—The pure ester (10 g.) in 50 g. of rectified spirit was treated with a solution of 9·6 g. of 96% potassium cyanide (2 mols.) in 20 g. of water. The mixture, which became warm, was kept for 48 hours, the alcohol was then distilled off, a very large excess of concentrated hydrochloric acid added, and the liquid heated under reflux for 3 hours, cooled, diluted with water, and extracted six times with ether after addition of ammonium sulphate. The *as*-dimethylsuccinic acid obtained from the extract (yield, 6·2 g. or 60%) melted, after crystallisation from concentrated hydrochloric acid, at 141°; m. p. of a mixture with an authentic specimen (Higson and Thorpe, J., 1906, **89**, 1465), 141—142°.

Ethyl as-*dimethylsuccinate* was prepared by heating a mixture of 8·0 g. of the crude acid, 40 g. of absolute alcohol, 40 g. of sodium-dried benzene, and 4 g. of concentrated sulphuric acid under reflux

for 5½ hours and was isolated, after the addition of water, from the benzene layer and an ethereal extract of the aqueous layer. It had b. p. 106—108°/20 mm. (yield, 6·9 g. or 62%). On redistillation, it had b. p. 101°/15 mm., $n_D^{27°}$ 1·4209, $d_4^{27°}$ 0·9945, $[R_L]_D$ 51·53 (calc., 51·69).

For purposes of comparison, ethyl succinate was prepared from Kahlbaum's succinic acid under similar conditions; the quantities employed were 15·0 g. of succinic acid, 75 g. of absolute alcohol, 75 g. of sodium-dried benzene, and 8 g. of concentrated sulphuric acid. The yield of ester, b. p. 102°/15 mm., at the first distillation was 16·3 g. or 74%. On redistillation, it boiled constantly at 103°/14 mm. and had $n_D^{21·6°}$ 1·4193, $d_4^{21·6°}$ 1·0384, whence $[R_L]_D$ 42·37 (calc., 42·45).

cyclo*Pentane Series.*

*cyclo*Pentanone was prepared by the catalytic decomposition of adipic acid (G.P., 1911, 256,622; Roger Adams, "Organic Syntheses," 1925, **5**, 37), but in view of its volatility in ether vapour the crude *cyclo*pentanone was separated from the small aqueous layer, neutralised with anhydrous potassium carbonate, and distilled; the pure ketone passed over at 130°/755 mm. A further small quantity was obtained from the aqueous layer by extraction with ether.

Ethyl *cyclo*pentylidenecyanoacetate (XII) was prepared by the condensation of equimolecular quantities of *cyclo*pentanone and ethyl cyanoacetate in the presence of piperidine (for conditions, see ethyl *cyclo*heptylidenecyanoacetate). The solid obtained when the product was poured into water contained a considerable quantity of oil (compare Harding and Haworth, J., 1910, **97**, 490); this was extracted with ether, washed in the ethereal solution with dilute hydrochloric acid and with water, dried with anhydrous sodium sulphate, and distilled; a mixture of *cyclo*pentanone and ethyl cyanoacetate passed over, followed by the ester (XII) as a viscid colourless oil which crystallised on cooling (yield, 55—60%).

Reduction with Moist Aluminium Amalgam. Preparation of Ethyl r-cyclo*Pentylcyanoacetate* (XIII).—The ester (50 g.) was reduced with 75 g. of aluminium amalgam under the usual conditions: there was a period of induction for 3 to 4 hours and the reaction was complete after 10 hours. On being worked up in the usual manner and distilled, the product gave *ethyl* r-cyclo*pentylcyanoacetate* (XIII), b. p. 130—131°/12 mm. (38·5 g.), and a high-boiling residue (XIV) (6·3 g.). The former on redistillation boiled at 129°/13 mm. and had $n_D^{19·2°}$ 1·4536, $d_4^{19·2°}$ 1·0242, $[R_L]_D$ 47·86 (calc., 47·65) (Found: C, 66·0; H, 8·2. $C_{10}H_{15}O_2N$ requires C, 66·3; H, 8·3%). The high-boiling residue, a very viscid reddish-brown oil, has not yet been

obtained crystalline. Its bimolecular character was established by a determination of its molecular weight in camphor by Houben's modification of Rast's method (*J. pr. Chem.*, 1923, **105**, 27) (Found: *M*, in camphor, 365. $C_{20}H_{28}O_4N_2$ requires *M*, 360). This and all the other bimolecular cyclic compounds are not readily hydrolysed and appear to have cyclic structures analogous to that of the reduction product of mesityl oxide with moist aluminium amalgam (compare Vogel, J., 1927, 594).

Hydrolysis of the Ester (XIII). *Preparation of* cyclo*Pentylmalonic Acid.*—The hydrolysis was carried out exactly as described under ethyl *iso*propylcyanoacetate. The quantities employed were 19 g. of ethyl *cyclo*pentylcyanoacetate, 40 g. of rectified spirit, 35 g. of caustic potash in 70 g. of water; the yield of the crude acid was almost quantitative. It separated from hot chloroform in small, glistening plates, m. p. 165° (decomp.) (Found: C, 55·6; H, 6·9; equiv., by titration, 86. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%; equiv., 86).

Condensation of Ethyl cyclo*Pentylidenecyanoacetate with Alcoholic Potassium Cyanide. Preparation of 1-Carboxy*cyclo*pentane-1-acetic Acid* (XV).—The condensation was carried out exactly as described for *as*-dimethylsuccinic acid: the quantities employed were 25·0 g of ester, 125 g. of rectified spirit, 20·5 g. (2 mols.) of 96% potassium cyanide in 45 g. of water; the yield of crude acid was 19·5 g. o 81%. The acid crystallised from concentrated hydrochloric acid in which it is much less soluble than the *gem*-dimethyl compound in small glistening prisms, m. p. 160° (Found: C, 55·8; H, 7·0 equiv., by titration, 86. Calc.: C, 55·8; H, 7·0%; equiv., 86). Th original specimen of Norris and Thorpe (J., 1921, **119**, 1209) wa found to melt at 154·5—155·5°: mixed m. p. 155—158°.

The *anhydride* was prepared in 90% yield by heating the crud acid with 4 mols. of acetyl chloride and removing the excess acetyl chloride in a vacuum over caustic potash. After two disti lations it boiled at 135—137°/13 mm. as a fairly viscid, colourle liquid which crystallised when left in contact with light petroleu (b. p. 40—60°); m. p. 32° (Found: C, 62·0; H, 6·4. C_8H_{10} requires C, 62·3; H, 6·6%).

The *anilic acid* was formed when the anhydride and aniline we warmed in benzene solution. After removal of the excess of anili in dilute hydrochloric acid, and spontaneous evaporation of t benzene layer, the residue was crystallised from dilute methyl alcoh the anilic acid separating in thin, feathery plates which melted 169° and decomposed with the evolution of steam at 170° (Foun C, 67·8; H, 7·1. $C_{14}H_{17}O_3N$ requires C, 68·0; H, 6·9%).

The *ethyl* ester was prepared exactly as described under et

as-dimethylsuccinate : the quantities employed were 7·0 g. of crude acid, 35 g. of absolute alcohol, 35 g. of sodium-dried benzene, and 3·5 g. of concentrated sulphuric acid. The yield of ester at the first distillation was 5·9 g. or 65%. On redistillation, the ester boiled at 129°/13 mm. and had $n_D^{20.2°}$ 1·4477, $d_4^{20.2°}$ 1·0412, $[R_L]_D$ 58·63 (calc., 58·72) (Found : C, 63·0; H, 8·9. $C_{12}H_{20}O_4$ requires C, 63·1; H, 8·9%).

cyclo*Hexane Series.*

Ethyl *cyclo*hexylidenecyanoacetate (XVI) was prepared by the condensation of pure *cyclo*hexanone and ethyl cyanoacetate in the presence of piperidine (Harding, Haworth, and Perkin, *loc. cit.*) in *ca.* 60% yield. The pure ester, thrice distilled under reduced pressure, boiled at 151°/12 mm. and had $n_D^{18.0°}$ 1·4974, $d_4^{18.0°}$ 1·0556, $[R_L]_D$ 53·57 (calc., 51·80). Lapworth and McRae give b. p. 160—163°/15 mm. (J., 1922, **121**, 2754); Birch, Kon, and Norris (J., 1923, **123**, 1373) give b. p. 151°/10 mm., $d_4^{19.5°}$ 1·05394, $n_D^{19.5°}$ 1·49670, which give $[R_L]_D$ 53·59 in good agreement with the value determined by the present author : the values $[R_L]_D$ 53·94 (calc., 51·59) given by the latter authors are erroneous.

Reduction with Moist Aluminium Amalgam. Preparation of Ethyl r-cyclo*Hexylcyanoacetate* (XVII).—The ester (100 g.) was reduced with 150 g. of aluminium amalgam; there was a period of induction of about 3 hours and the reaction was complete after 9 hours. When the product was worked up in the usual manner and distilled, *ethyl* r-cyclo*hexylcyanoacetate* (XVII) (85 g.) passed over at 144—146°/14 mm.: the viscid residue was dissolved in methyl alcohol, the solvent evaporated in a vacuum over concentrated sulphuric acid, and traces of impurities removed by repeated extraction with boiling light petroleum (b. p. 40—60°); the product crystallised completely when left in a vacuum over concentrated sulphuric acid for 24 hours (yield, 6 g.). It melted at 87° and was the bimolecular *cyano-ester* (XVIII) (Found : *M*, in camphor, 396. $C_{22}H_{32}O_4N_2$ requires *M*, 388). The liquid reduction product on redistillation boiled at 145°/14 mm., and had $n_D^{18.5°}$ 1·4612, $d_4^{18.5°}$ 1·0221, whence $[R_L]_D$ 52·39 (calc., 52·21) (Found : C, 67·5; H, 8·5. $C_{11}H_{17}O_2N$ requires C, 67·8; H, 8·7%).

Hydrolysis of the Ester (XVII). *Preparation of* cyclo*Hexylmalonic Acid.*—The hydrolysis was carried out as described under ethyl *iso*propylcyanoacetate and was considered to be complete after 18 hours. The quantities employed were 20 g. of ethyl *cyclo*hexylcyanoacetate, 40 g. of rectified spirit, and 30 g. of potassium hydroxide in 60 g. of water. The acid, which was obtained in practically quantitative yield, separated from acetone–chloroform in feathery plates, m. p. 178° (decomp.), and its identity with

*cyclo*hexylmalonic acid was established by direct comparison with an authentic specimen, m. p. 176—177° (decomp.), synthesised from bromo*cyclo*hexane and ethyl sodiomalonate; mixed m. p. 177—178° (decomp.).

The condensation of ethyl *cyclo*hexylidenecyanoacetate with alcoholic potassium cyanide had previously been carried out by Lapworth and McRae (J., 1922, **121**, 2754): the quantities here employed were 30 g. of ester, 150 g. of rectified spirit, and 21·1 g. (2 mols.) of 96% potassium cyanide in 45·5 g. of water. Hydrolysis was effected by boiling under reflux with a large excess of concentrated hydrochloric acid for 6 hours: the use of fuming hydrochloric acid (Lapworth and McRae) seems unnecessary. The 1-carboxy-*cyclo*hexane-1-acetic acid (yield, 24·7 g. or 86%) crystallised from concentrated hydrochloric acid in flat prisms, m. p. 134°, but was less soluble than the corresponding *gem*-dimethyl and *cyclo*pentane compounds. It may also be crystallised from chloroform–light petroleum (b. p. 40—60°). Its constitution was confirmed by a comparison with the original specimen of Norris and Thorpe (J., 1921, **119**, 1206), m. p. 132°, mixed m. p. 133—134°. The anhydride, prepared in 92% yield by the method described for the *cyclo*pentane analogue, crystallised from light petroleum (b. p. 40—60°) in plates, m. p. 56° (Norris and Thorpe, *loc. cit.*, give m. p. 57°). The anilic acid, prepared from the anhydride and aniline in benzene solution, crystallised from dilute methyl alcohol in lustrous, glistening plates, m. p. 181° (decomp.) (Norris and Thorpe, *loc. cit.*, give m. p. 180°).

cyclo*Heptane Series.*

Ethyl cyclo*Heptylidenecyanoacetate* (XX).—Suberone, b. p. 181°/769 mm., was prepared in 35—40% yield by the dry distillation of thorium suberate (Ruzicka, *Helv. Chim. Acta*, 1926, **9**, 515); and later by the catalytic decomposition of suberic acid, full details of which are given in the following communication.

A mixture of the ketone (44 g.), ethyl cyanoacetate (46 g.), and piperidine (1 g.) was after 48 hours heated on a steam-bath for 4 hours, cooled, and poured into water. The heavy oil produced was isolated by means of ether and, after the usual washing and drying, was distilled; suberone and ethyl cyanoacetate passed over first, and then the *cyano-ester* (XX) at 162—163°/14 mm. (yield, 27·3 g. or 31%). By treating the low fraction with a large excess of saturated aqueous-alcoholic sodium bisulphite solution (Ruzicka and Brugger, *Helv. Chim. Acta*, 1926, **9**, 339), 18 g. of pure suberone were recovered. On redistillation the ester boiled at 160°/12 mm. and had $n_D^{15·6°}$ 1·5003, $d_4^{15·6°}$ 1·0534, $[R_L]_D$ 57·86 (calc., 56·62) (Found: C, 69·4; H, 8·2. $C_{12}H_{17}O_2N$ requires C, 69·5; H, 8·3%).

Reduction with Moist Aluminium Amalgam. Preparation of Ethyl r-cyclo*Heptylcyanoacetate* (XXI).—17·2 G. of ethyl *cyclo*heptylidenecyanoacetate were treated with 35 g. of moist aluminium amalgam in ether; there was a period of induction for several hours and the reduction was considered complete after 18 hours. The product was isolated in the usual manner and distilled, *ethyl* r-cyclo*heptylcyanoacetate* (12·4 g.) passing over at 152—154°/12 mm., mainly at 152°/12 mm. The residue, which solidified to a transparent glassy solid on cooling, was treated several times with boiling light petroleum (b. p. 40—60°) to remove impurities; it crystallised after being left in a vacuum over concentrated sulphuric acid for 48 hours (yield, 2·1 g.). It had m. p. 74° and was the bimolecular compound (XXII) (Found: *M*, in camphor, 418. $C_{24}H_{36}O_4N_2$ requires *M*, 416). The liquid reduction product on redistillation boiled at 149°/11 mm. and had $n_D^{19.0°}$ 1·4664, $d_4^{19.7°}$ 1·0209, whence $[R_L]_D$ 56·78 (calc., 56·89) (Found: C, 68·7; H, 9·1. $C_{12}H_{19}O_2N$ requires C, 68·9; H, 9·2%).

Hydrolysis of the Ester (XXI). *Preparation of* cyclo*Heptylmalonic Acid*.—The hydrolysis was effected as described under ethyl *iso*propylcyanoacetate, the quantities employed being 6·5 g. of ethyl *cyclo*heptylcyanoacetate, 13 g. of rectified spirit, and 7·0 g. (4 mols.) of potassium hydroxide in 14 g. of water. The crude acid was only sparingly soluble in chloroform but crystallised from benzene–acetone in thin plates, m. p. 164·5° (decomp.) (Found: C, 60·0; H, 7·9. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%).

Condensation of Ethyl cyclo*Heptylidenecyanoacetate with Alcoholic Potassium Cyanide. Preparation of* 1-*Carboxy*cyclo*heptane*-1-*acetic Acid* (XXIII).—The reaction was carried out as described for *as*-dimethylsuccinic acid: the quantities employed were 12 g. of the ester (XX), 60 g. of rectified spirit, and 8·1 g. (2 mols.) of 96% potassium cyanide in 18 g. of water (yield of crude acid, 9·9 g. or 86%). 1-Carboxy*cyclo*heptane-1-acetic acid is very sparingly soluble in concentrated hydrochloric acid, probably less so than its *cyclo*pentane analogue; it crystallises from dilute hydrochloric acid in small prisms, m. p. 159° (Found: C, 60·0; H, 8·0; equiv., by titration, 100. Calc.: C, 60·0; H, 8·0%; equiv., 100); Dickens, Horton, and Thorpe (*loc. cit.*) give m. p. 153°. The *anhydride*, m. p. 16°, b. p. 166°/13 mm., obtained in excellent yield by treatment of the crude acid with acetyl chloride, was converted in the usual manner into the *anilic acid*, which separated from dilute methyl alcohol in feathery plates, m. p. 159°, decomp. 160° (Found: C, 69·1; H, 7·6. $C_{16}H_{21}O_3N$ requires C, 69·3; H, 7·7%).

trans-*Decahydro-β-naphthalene Series.*

trans-Decahydro-β-naphthol (*trans*-β-decalol) was obtained from the " Dekahydro-β-naphthol rein " of the Deutsche Hydrierwerke Aktiengesellschaft by spreading the oily sticky solid, which probably consisted of a mixture of the *cis*- and *trans*-isomerides, on large porous plates: the resultant crystalline solid melted at 74° (Hückel, *Annalen*, 1925, **441**, 18, gives m. p. 75° for pure *trans*-β-decalol). The alcohol was dissolved in three times its weight of glacial acetic acid and gradually treated, under reflux, with half its weight of recrystallised chromic acid dissolved in the minimum quantity of water. When the initial vigorous reaction had subsided the whole was warmed on the steam-bath for 30 minutes and steam-distilled. The mixture of *trans*-β-decalone (which is only moderately easily volatile in steam) and acetic acid isolated from the distillate by means of ether (three extractions) was shaken for 1 hour with a large excess of saturated aqueous-alcoholic sodium bisulphite solution (Ruzicka and Brugger, *Helv. Chim. Acta*, 1926, **9**, 339). The bisulphite compound, which separated as a silky crystalline solid, was collected and decomposed with an excess of sodium hydroxide solution, and the *trans*-β-decalone isolated by extraction (twice) with ether. It distilled at 106°/12 mm. as a colourless, somewhat viscid liquid with a characteristic odour and had $d_4^{17.7°}$ 0·9800, $n_D^{17.7°}$ 1·4843, whence $[R_L]_D$ 44·44 (calc., 43·99) (Hückel, *loc. cit.*, gives for *trans*-β-decalone regenerated from the semicarbazone, $d_4^{20°}$ 0·975, $n_D^{19.0°}$ 1·48088). The yield of pure *trans*-β-decalone from 87 g. of *trans*-β-decalol was 48 g.

Ethyl trans-*Decahydro-β-naphthylidenecyanoacetate* (XXIV).—A mixture of 35·0 g. of pure *trans*-β-decalone, 26·5 g. of ethyl cyanoacetate, and 1 g. of piperidine was after 24 hours heated on the steam-bath for 6 hours. Ether was then added and the product was washed with dilute hydrochloric acid and with water and dried with anhydrous sodium sulphate. The residue after evaporation of the ether was fractionated: unchanged *trans*-β-decalone and ethyl cyanoacetate were first collected and the condensation product passed over at 190—205°/15 mm. The last on refractionation distilled at 197°/14 mm. (Found: C, 72·8; H, 8·5. $C_{15}H_{21}O_2N$ requires C, 72·8; H, 8·6%) and had $d_4^{19.4°}$ 1·0523, $n_D^{19.4°}$ 1·5108, whence $[R_L]_D$ 70·34 (calc., 68·08). Yield, 47 g. or 61%.

Reduction with Moist Aluminium Amalgam. Preparation of Ethyl r-trans-*Decahydro-β-naphthylcyanoacetate* (XXV or XXVI).—35·0 G. of the unsaturated cyano-ester (XXIV) were treated with 70 g. of moist aluminium amalgam in ether: there was a period of induction of at least 8 hours and the reduction was complete after 22 hours. The product was isolated in the usual manner and dis-

tilled and the following fractions were collected: (1) B. p. 184°/12 mm.; this had $n_D^{18.9°}$ 1·4811, $d_{4°}^{18.9°}$ 1·0263. (2) A large middle fraction, b. p. 184—186°/12 mm., mainly 186°/12 mm., $n_D^{19.9°}$ 1·4802, $d_{4°}^{19.9°}$ 1·0302, whence $[R_L]_D$ 68·73 (calc., 68·54). (3) A small tail fraction, b. p. 186—187°/12 mm., $n_D^{19.3°}$ 1·4805, $d_{4°}^{19.3°}$ 1·0297. Total yield, 27·5 g. The distillate was obviously homogeneous and on redistillation boiled constantly at 186°/12 mm. (Found: C, 72·4; H, 9·2. $C_{15}H_{23}O_2N$ requires C, 72·3; H, 9·3%): no trace of a second isomeride could be detected by distillation. The residue was a very viscid yellow oil which did not crystallise when left for a week over concentrated sulphuric acid in a vacuum: yield, 2·5 g. (Found: M, in camphor, 488. $C_{30}H_{44}O_4N_2$ requires M, 496).

Hydrolysis with Alcoholic Potassium Hydroxide. Preparation of trans-*Decahydro-β-naphthylmalonic Acid.*—A mixture of 8·3 g. of the ester (b. p. 186°/12 mm.) in 16 g. of rectified spirit and 7·5 g. of potassium hydroxide in 15 g. of water was refluxed for 18 hours and then evaporated to dryness on the steam-bath. The residue was triturated with ether to remove unchanged ester, if any, and acidified with very dilute sulphuric acid, a sticky solid separating. The whole was extracted three times with ether: the ethereal solution, which soon deposited a crystalline acid, m. p. 122° (decomp.), was slightly concentrated, and the separated acid collected: this process was repeated five times until practically all the ether had been evaporated. The acid which separated at each crystallisation melted at 122° (decomp.) and the total yield was nearly quantitative (Found: C, 65·3; H, 8·1. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·4%). No isomeric acid was isolated. The acid crystallises from benzene or acetone–chloroform as a microcrystalline powder, m. p. 122° (decomp.).

Determinations of Surface Tension and of Density over a Range of Temperatures. Calculation of the Parachor.

The surface tension was determined by the method of Richards, Speyers, and Carver (*J. Amer. Chem. Soc.*, 1924, **46**, 1196) in an apparatus constructed entirely of Pyrex glass. Two capillary tubes of diameters approximately 0·5 mm. and 2 mm. respectively, of nearly circular cross-section and of uniform bore were joined together to form a U-tube, which was provided with a small opening at its lowest point. The U-tube was fused in a vertical position to the inside of a thin-walled glass cylinder, and this was fused to a larger tube, which could be surrounded by the vapour of boiling chloroform (*ca.* 61°) or trichloroethylene (*ca.* 86°); the exact temperature was indicated by a small standard Anschütz thermometer graduated in fifths of a degree. The difference in capillary rise was

measured by means of a travelling microscope capable of reading directly to 0·02 mm. and by estimation to 0·01 mm. and provided with a 5-inch objective, for the construction of which the author is indebted to Mr. W. J. Colebrooke of the Physics Department of this College; it enabled both meniscuses to be observed simultaneously.

The apparatus was cleaned by being immersed in chromic acid mixture for 6 hours, washed with water, rectified spirit, and pure sodium-dried ether, and dried in the steam-oven. It was standardised with conductivity water, prepared in a modified Bourdillon still, in the manner suggested by Richards, Speyers, and Carver (*loc. cit.*).

The measurements of capillary rise for each liquid (about 3 c.c.) were made with the usual precautions. The vertical cross-wire in the eye-piece of the microscope was adjusted parallel to and approximately mid-way between the capillary tubes. At least six readings of each meniscus were taken from several directions, so as to minimise the effect of possible imperfections in the glass, the exact temperature at each adjustment being observed.

The corrections for the meniscus, determined by Poisson's equation $h_1 = h + r/3 - 0{\cdot}1288\ r^2/h$, where h_1 is the corrected capillary rise, h is the observed capillary rise, and r is the radius of the tube (Richards, Speyers, and Carver, *loc. cit.*), were 0·245 mm. for liquids of the water type ($h = ca.$ 50 mm.) and $-$ 0·234 mm. for most organic liquids ($h = ca.$ 25 mm.). Throughout the present paper, the corrected difference in height between the meniscuses in the capillary tubes, H, is obtained from the observed difference, h (expressed in mm.), by subtracting 0·24. The constant of the apparatus, K, was obtained from the equation $\gamma = KHd$, where γ and d are respectively the surface tension and the density at the same temperature; the surface tension of water at 20° was taken as 72·80 (Harkins and Brown, *J. Amer. Chem. Soc.*, 1919, **41**, 499), and the temperature coefficient 0·15 dyne $cm.^{-1}$ (degree $Cent.)^{-1}$ (compare Ferguson and Vogel, *Proc. Physical Soc.*, 1926, **38**, 193). The mean of several concordant determinations gave $K = 1{\cdot}8805$.

The densities were determined with a pyknometer of about 1·5 c.c. capacity, carefully calibrated with conductivity water. The pyknometer was completely surrounded by a closely fitting, double-walled glass vessel, the annular space being filled with a suitable vapour.

In the tables, t is the temperature, h the observed difference in height, expressed in mm., of the liquid in the two arms of the U-tube, H the corrected value, $d_{4^\circ}^{t^\circ}$ the density (in g./c.c.) calculated from the observed densities by assuming a linear variation with temperature, and γ the surface tension, expressed in dynes/cm., computed from

the equation $\gamma = KHd$. The parachor in the last column has been derived from the expression $[P] = \gamma^{\frac{1}{4}}M/d_{4^\circ}^{t^\circ}$, where M is the molecular weight; the density of the vapour has been neglected.

Except where stated otherwise, the liquids were thrice distilled under diminished pressure before use.

Ethyl r-iso*propylcyanoacetate*, $M = 155{\cdot}10$, b. p. 99°/16 mm. Densities determined: $d_{4^\circ}^{19\cdot2^\circ}$ 0·9862, $d_{4^\circ}^{62\cdot4^\circ}$ 0·9481, $d_{4^\circ}^{86\cdot8^\circ}$ 0·9261.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	Parachor.
23·3°	17·28	17·04	0·9826	31·49	373·9
61·8	15·71	15·47	0·9486	27·60	374·8
86·6	14·78	14·54	0·9261	25·32	375·7
					Mean 374·8

Ethyl r-cyclo*pentylcyanoacetate*, $M = 181{\cdot}13$, b. p. 129°/13 mm. Densities determined: $d_{4^\circ}^{17\cdot7^\circ}$ 1·0263, $d_{4^\circ}^{61\cdot6^\circ}$ 0·9936, $d_{4^\circ}^{86\cdot2^\circ}$ 0·9714.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	Parachor.
17·7°	18·37	18·13	1·0263	34·99	429·2
61·2	16·77	16·53	0·9932	30·87	429·9
86·4	15·89	15·65	0·9712	28·58	431·2
					Mean 430·1

Ethyl r-cyclo*hexylcyanoacetate*, $M = 195{\cdot}13$, b. p. 145°/14 mm. Densities determined: $d_{4^\circ}^{18\cdot5^\circ}$ 1·0221, $d_{4^\circ}^{61\cdot2^\circ}$ 0·9901, $d_{4^\circ}^{86\cdot4^\circ}$ 0·9690.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	Parachor.
17·3°	18·87	18·63	1·0229	35·84	466·8
61·8	17·22	17·98	0·9897	31·60	467·5
85·6	16·34	16·10	0·9696	29·36	468·5
					Mean 467·6

Ethyl r-cyclo*heptylcyanoacetate*, $M = 209{\cdot}15$, b. p. 149°/11 mm. Densities determined: $d_{4^\circ}^{19\cdot7^\circ}$ 1·0209, $d_{4^\circ}^{60\cdot8^\circ}$ 0·9898, $d_{4^\circ}^{86\cdot6^\circ}$ 0·9704.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	Parachor.
21·3°	19·04	18·80	1·0197	35·96	502·3
61·8	17·46	17·22	0·9898	32·05	502·8
86·0	16·53	16·29	0·9708	29·74	503·1
					Mean 502·7

Ethyl trans-r-*decahydro*-β-*naphthylcyanoacetate*, $M = 249{\cdot}19$, b. p. 186°/14 mm. Densities determined: $d_{4^\circ}^{19\cdot9^\circ}$ 1·0302, $d_{4^\circ}^{60\cdot2^\circ}$ 1·0011, $d_{4^\circ}^{84\cdot8^\circ}$ 0·9861.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	Parachor.
20·1°	18·99	18·75	1·0301	36·32	593·9
60·8	17·65	17·41	1·0021	32·81	595·1
84·1	16·82	16·58	0·9866	30·76	594·8
					Mean 594·6

cyclo*Pentanone*, $M = 84{\cdot}06$. The middle fraction, b. p. 130·5°/765·5 mm., collected from the distillation of a large quantity of *cyclo*pentanone prepared from adipic acid was added to a large excess of saturated aqueous-alcoholic sodium bisulphite solution, the

bisulphite compound, which slowly separated in thin, silky plates, was removed and treated with an excess of a concentrated sodium carbonate solution, and the ketone was separated by steam-distillation and extraction (twice) with ether. The extracts were dried with anhydrous sodium sulphate and the ether was *slowly* distilled through a long column. The residue, after being twice fractionated under atmospheric pressure, boiled at 129·5°/761·5 mm. The pure ketone had $n_D^{16·0°}$ 1·4383, $d_{4°}^{16·0°}$ 0·9524, whence $[R_L]_D$ 23·18 (calc., 23·10) (Wallach, *Annalen*, 1907, **353**, 331, gives $d^{20°}$ 0·948, n_D 1·4366, $[R_L]_D$ 23·19).

Densities determined: $d_{4°}^{16·4°}$ 0·9518, $d_{4°}^{62·8°}$ 0·9099, $d_{4°}^{86·4°}$ 0·8871.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	Parachor.
18·0°	19·31	19·07	0·9504	34·08	213·7
61·6	17·19	16·95	0·9110	29·04	214·2
85·4	16·05	15·81	0·8880	26·40	214·6
					Mean 214·2

cyclo*Hexanone*, *M* = 98·08. Boot's pure *cyclo*hexanone was purified through the bisulphite compound by the method described under *cyclo*pentanone; after being distilled twice under reduced pressure, it boiled at 47°/15 mm. and had $d_{4°}^{16·9°}$ 0·9488, $n_D^{16·9°}$ 1·4521, whence $[R_L]_D$ 27·89 (calc., 27·72) (Wallach, *loc. cit.*, gives $d^{21°}$ 0·947, n_D 1·4503, $[R_L]_D$ 27·82).

Densities determined: $d_{4°}^{15·7°}$ 0·9492, $d_{4°}^{59·8°}$ 0·9116, $d_{4°}^{86·0°}$ 0·8902.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	Parachor.
17·3°	19·77	19·53	0·9479	34·81	251·3
61·6	17·64	17·40	0·9118	29·84	251·4
86·4	16·44	16·20	0·8899	27·11	251·5
					Mean 251·4

cyclo*Heptanone*, *M* = 112·10. Suberone, b. p. 181°/769 mm., prepared from thorium suberate was purified through the bisulphite compound. The regenerated ketone had a pleasant odour which was somewhat like that of peppermint and quite different from the "hydrocarbon" odour of the ketone isolated directly from thorium suberate. It boiled at 71°/19 mm. during two distillations under reduced pressure and had $n_D^{15·0°}$ 1·4635, $d_{4°}^{15·0°}$ 0·9526, whence $[R_L]_D$ 32·44 (calc., 32·34) (Wallach, *loc. cit.*, gives $d^{21°}$ 0·9500, n_D 1·4604, $[R_L]_D$ 32·32).

Densities determined: $d_{4°}^{15·6°}$ 0·9507, $d_{4°}^{59·7°}$ 0·9160, $d_{4°}^{86·5°}$ 0·8954.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	Parachor.
19·9°	20·05	19·81	0·9497	35·38	287·9
61·6	18·12	17·88	0·9161	30·80	288·3
86·4	16·84	16·60	0·8957	27·96	287·8
					Mean 288·0

trans-β-*Decalone*, *M* = 152·13. The specimen employed was purified through the bisulphite compound and was twice distilled

under diminished pressure. It boiled at 106°/12 mm. and had $d_{4^\circ}^{17.7^\circ}$ 0·9800, $n_D^{17.7^\circ}$ 1·4843, whence $[R_L]_D$ 44·44 (calc., 43·99) (Hückel, *Annalen*, 1925, **441**, 1, gives $d_{4^\circ}^{20^\circ}$ 0·975, $n_D^{19^\circ}$ 1·48088, $[R_L]_D$ 44·34).

Densities determined: $d_{4^\circ}^{17.9^\circ}$ 0·9802, $d_{4^\circ}^{62.2^\circ}$ 0·9493, $d_{4^\circ}^{85.3^\circ}$ 0·9331.

t.	*h.*	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	Parachor.
19·3°	20·14	19·90	0·9792	36·64	382·2
61·8	18·39	18·17	0·9496	32·45	382·3
85·1	17·55	17·31	0·9332	30·38	382·7
					Mean 382·4

Ethyl cyclo*hexylidenecyanoacetate*, M = 193·13, b. p. 151°/12 mm. Densities determined: $d_{4^\circ}^{18.5^\circ}$ 1·0570, $d_{4^\circ}^{62.1^\circ}$ 1·0211, $d_{4^\circ}^{85.4^\circ}$ 1·0030.

t.	*h.*	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	Parachor.
18·1°	19·37	19·13	1·0573	38·04	453·6
61·8	17·80	17·56	1·0213	33·73	455·6
85·0	16·87	16·63	1·0033	31·38	455·6
					Mean 454·7

Ethyl cyclo*heptylidenecyanoacetate*, M = 207·14, b. p. 160°/12 mm. Densities determined: $d_{4^\circ}^{18.3^\circ}$ 1·0564, $d_{4^\circ}^{61.6^\circ}$ 1·0219, $d_{4^\circ}^{85.6^\circ}$ 1·0037.

t.	*h.*	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	Parachor.
18·6°	19·25	19·01	1·0546	37·70	486·7
62·0	17·73	17·49	1·0216	33·60	488·1
85·4	16·86	16·62	1·0039	31·37	488·3
					Mean 487·7

Ethyl trans-*decahydro-β-naphthylidenecyanoacetate*, M = 247·18, b. p. 196°/14 mm. Densities determined: $d_{4^\circ}^{19.1^\circ}$ 1·0523, $d_{4^\circ}^{60.3^\circ}$ 1·0239, $d_{4^\circ}^{85.0^\circ}$ 1·0091.

t.	*h.*	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	Parachor.
21·6°	19·15	18·91	1·0508	37·37	581·6
61·8	17·86	17·62	1·0242	33·94	582·5
85·0	17·14	16·90	1·0091	32·07	582·9
					Mean 582·3

Ethyl benzylidenemalonate, M = 248·13, b. p. 179·5°/14 mm. Densities determined: $d_{4^\circ}^{18.5^\circ}$ 1·1049 (supercooled liquid), $d_{4^\circ}^{61.4^\circ}$ 1·0708, $d_{4^\circ}^{84.0^\circ}$ 1·0528.

t.	*h.*	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	Parachor.
19·8°	18·88	18·64	1·1039	38·70	560·6
61·2	17·33	17·09	1·0710	34·42	561·2
84·3	16·49	16·25	1·0527	32·17	561·4
					Mean 561·1

Ethyl benzylmalonate, M = 250·14, b. p. 163°/14 mm. Densities determined: $d_{4^\circ}^{19.7^\circ}$ 1·0761, $d_{4^\circ}^{61.2^\circ}$ 1·0433, $d_{4^\circ}^{86.0^\circ}$ 1·0231.

t.	*h.*	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	Parachor.
20·5°	17·81	17·57	1·0755	35·54	567·9
61·2	16·24	16·00	1·0433	31·39	567·6
83·5	15·39	15·15	1·0243	29·18	567·6
					Mean 567·7

In conclusion, the author wishes to express his indebtedness to Professor J. F. Thorpe, F.R.S., for his kind encouragement and advice, to Dr. S. Sugden for his criticism of the parachor results, to the Trustees of the Beit Scientific Research Fellowships for a Fellowship, and to the Chemical Society and the Royal Society for grants which have defrayed part of the heavy cost of this research.

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CCLXIII.—*Syntheses of Cyclic Compounds. Part IV. The Catalytic Decomposition of Suberic Acid and the Preparation of Suberone directly from Mixtures of Suberic and Azelaic Acids.*

By ISRAEL VOGEL.

IT is proposed to investigate the decomposition, in the presence of various catalysts, of both simple and substituted dibasic acids in order (1) to develop simple methods for the preparation of cyclic ketones and (2) to study the effect of substituents on this method of ring formation. The present communication is concerned with suberic acid. The only previous work on this subject (D.R.-P. 256622) was the alleged production of suberone in good yield by the dry distillation of suberic acid in the presence of 5% by weight of iron filings; Aschan (*Ber.*, 1912, **45**, 1603), however, isolated a small quantity of suberone by the dry distillation of the acid. Day, Kon, and Stevenson (J., 1920, **117**, 639) were unable to obtain satisfactory results by this catalytic process and reverted to the dry distillation of the calcium salt as a method for the preparation of suberone.

The author finds that if an intimate mixture of suberic acid, an *equal weight* of iron filings (a quantity considerably greater than the equivalent quantity), and 5% by weight of crystallised baryta be subjected to dry distillation, a yield approaching 40% of suberone is obtained. The crude product is an almost colourless, mobile liquid with a characteristic ketonic odour in contrast with the practically black liquid, contaminated with suspended matter and having a characteristic " hydrocarbon " odour, obtained from either the calcium or the thorium salt.

The mixture of azelaic and suberic acids obtained by the oxidation of ricinoleic acid with nitric acid (Day, Kon, and Stevenson, *loc. cit.*; Baker and Ingold, J., 1923, **123**, 122) also gives a good yield of

suberone, together with a relatively small quantity of a liquid the exact composition of which has not yet been elucidated. This liquid boils at about the same temperature as suberone but can readily be separated from it, as the latter reacts immediately with a saturated aqueous or preferably aqueous-alcoholic sodium bisulphite solution, whereas the former gives no solid derivative.

The formation of suberone by the catalytic decomposition of suberic acid probably takes place in two stages, involving the formation of the anhydride (I) and the subsequent elimination

$$\text{(I.)}\quad \left.\begin{array}{l} CH_2\cdot CH_2\cdot CH_2\cdot CO \\ CH_2\cdot CH_2\cdot CH_2\cdot CO \end{array}\right\rangle O \longrightarrow CO_2 + \left.\begin{array}{l} CH_2\cdot CH_2\cdot CH_2 \\ CH_2\cdot CH_2\cdot CH_2 \end{array}\right\rangle CO \quad \text{(II.)}$$

of carbon dioxide (compare Blanc, *Bull. Soc. chim.*, 1908, **3**, 778). Two other mechanisms are possible, one represented by (A) (compare Aschan, *loc. cit.*) and the other involving the intermediate formation of an iron salt.

$$\text{(A.)}\quad \begin{array}{l} CH_2\cdot CH_2\cdot CH_2\cdot CO_2H \\ CH_2\cdot CH_2\cdot CH_2\cdot CO_2H \end{array} \longrightarrow \begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot CO_2H \\ CH_2\cdot CH_2\cdot CH_2 > CO \end{array} \xrightarrow{-CO_2} \text{(II.)}$$

It is extremely difficult to prepare pure azelaic acid in quantity from the mixed acids obtained by the oxidation of ricinoleic acid with nitric acid; although a product, m. p. 106°, may be obtained by fractional crystallisation from solvents, this contains a considerable quantity of suberic acid, as was shown by analysis and by the production of suberone by its catalytic decomposition. Pure azelaic acid is best prepared by the oxidation of ricinoleic acid with potassium permanganate (Maquenne, *Bull. Soc. chim.*, 1899, **21**, 1061): this melted at 107° and no suberone was obtained by its catalytic decomposition.

EXPERIMENTAL.

Preparation of Suberic Acid.—Castor oil, in lots of 25 kg., was hydrolysed by alcoholic sodium hydroxide to ricinoleic acid, and the latter oxidised by nitric acid to a mixture of azelaic and suberic acids (Baker and Ingold, J., 1923, **123**, 122). The two acids were separated from each other by means of a mixture of benzene and ethyl alcohol in proportion intermediate between those described by Baker and Ingold (*loc. cit.*) and by Day, Kon, and Stevenson (*loc. cit.*); rectified spirit was substituted for absolute ethyl alcohol. The acid which first separated melted at 135—138° and after two crystallisations from water melted sharply at 140°.

Catalytic Decomposition of Suberic Acid.—An intimate mixture of 100 g. of suberic acid (m. p. 140°), 100 g. of iron filings, and 5 g. of finely powdered, crystallised barium hydroxide was placed in a

2-litre Pyrex distilling-flask fitted with a thermometer, reaching to within 0·5 cm. of the bottom, and connected with a long water-condenser and a receiver. The mixture was slowly heated in an air-bath, the space between the sides of the flask and the bath having been packed with copper turnings. Considerable frothing took place at about 235° and water distilled over: a mobile, slightly coloured liquid with a ketonic odour passed over at 280—290°. The ketone was separated from the water in the distillate, the aqueous layer was extracted twice with ether, and the combined extracts and ketone were washed with alkali and dried with anhydrous potassium carbonate. The ether having been removed through a long fractionating column, the residue was separated under reduced pressure into the following fractions: (1) a small head fraction, b. p. 63—65°/15 mm., $n_D^{18·1°}$ 1·4595, $d_{4°}^{18·1°}$ 0·9378; (2) a main fraction, b. p. 65·5—66°/15 mm., $n_D^{18·3°}$ 1·4611, $d_{4°}^{18·3°}$ 0·9467; (3) a small tail fraction, b. p. 67—70°/15 mm., $n_D^{17·8°}$ 1·4627, $d_{4°}^{17·8°}$ 0·9458. The residue weighed less than 1 g. and the total yield of distillate was 24 g. All the fractions were colourless mobile liquids, and remained so after being kept for 6 months (compare the product from calcium or thorium suberate which rapidly darkens on keeping), and on treatment with aqueous semicarbazide acetate and methyl alcohol gave immediate precipitates of semicarbazones which melted at 162—163°, either alone or when mixed with an authentic specimen of suberone semicarbazone prepared from thorium suberate, after one crystallisation from dilute methyl alcohol. No other semicarbazone could be isolated and it was evident that the ketone was practically pure *cyclo*heptanone. It could be obtained perfectly pure by regeneration from the bisulphite compound.

Preparation of Suberone from Mixtures of Suberic and Azelaic Acids.—The crude mixture of acids must first be recrystallised from benzene. An intimate mixture of 300 g. of the mixed acids, 300 g. of iron filings, and 15 g. of finely ground, crystallised barium hydroxide was distilled from a 4-litre Pyrex distilling flask as described for suberic acid. (The heating must be very gradual, as there is considerable frothing and evolution of fumes in the early part of the reaction—temperature 200—250°. Indeed, this part of the process may be conducted in the open on a large iron plate: the intimate mixture is gently heated until the evolution of steam and other fumes has ceased, and the cold dark-coloured product is broken up and transferred to the distilling flask.) The rate of heating was such that the liquid distilled at the rate of about one drop per second; the final temperature was 360—400°. The product was isolated as described under suberic acid and distilled, and the fraction, b. p. 62—75°/14 mm., collected; the yield averaged

90 g. from 600 g. of the mixed acids. This fraction was added to a saturated aqueous-alcoholic sodium bisulphite solution, and the crystalline bisulphite compound, which was immediately precipitated, was filtered off, well washed with alcohol and ether, and decomposed with sodium hydroxide, and the ketone isolated by ether extraction. Further small quantities of suberone may be obtained by treating the high-boiling fractions with sodium bisulphite.

The author wishes to thank Professor J. F. Thorpe, F.R.S., for his interest in these experiments and to state that this work is being published during the tenure of a Beit Scientific Research Fellowship.

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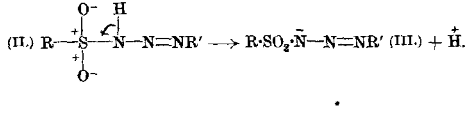
CCLXIV.—*The Action of Diazo-salts on Aromatic Sulphonamides. Part II. The Mechanism of the Reaction and the Constitution of the Diazo-sulphonamides.*

By ARTHUR KEY and PAVITRA KUMAR DUTT.

THE object of this investigation was to elucidate the mechanism of the reaction

$$R{\cdot}SO_2{\cdot}NH_2 + R'{\cdot}N_2X \longrightarrow R{\cdot}SO_2{\cdot}NH{\cdot}N{:}NR' \longrightarrow R{\cdot}SO_2H + R'N_3 \quad \text{(I.)}$$

(Dutt, Whitehead, and Wormall, J., 1921, **119**, 2088; Dutt, J., 1924, **125**, 1463), which takes place with extreme facility in the presence of alkali even at very low temperatures. Several examples of the formation of sulphinic acids under comparable conditions from other sulphonamide derivatives have also been recorded by Forster and Kunz (J., 1914, **105**, 1720) and by Holmes and Ingold (J., 1926, 1305). These reactions are apparently similar in their mechanism, being probably due to the action of hydroxyl ions on the hydrogen which is incipiently ionised because of the strong electron attraction exercised by some neighbouring centre (Holmes and Ingold, *loc. cit.*). For example, in the case of the diazo-sulphonamide (II) such electron attraction actuated by the neighbouring positive charges should induce it to ionise into the complex ion (III) and H^+.



After the removal of the proton as water the complex ion (III) should then undergo further change due to the proximity of the *positively charged sulphur; the latter would appropriate the two* electrons between the sulphur and the nitrogen, resulting in its fission into the sulphinate ion $R{\cdot}SO_2{}'$ and $R'N_3$. According to this *scheme the residue* $R'{-}\ddot{N}{=}\ddot{N}{-}\underset{\cdot\cdot}{\ddot{N}}$ should by subsequent movement of electrons be capable of existing in one of the two forms $R'{-}N{=}\overset{+}{N}{=}\overset{-}{N}$ and $R'{-}\overset{-}{N}{-}\overset{+}{N}{\equiv}N$. The distinction of any of these forms from the third possible formula for azoimide, $R'N{<}\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix}$, may perhaps be elucidated by parachor determination.

The reaction (I) may, on the other hand, be a case of true migration of the hydrogen atom from the nitrogen to the oxygen, followed by fission into the two final products. This hypothesis was tested by heating the pure dry sulphonamide ($R = p$-tolyl and $R' = Ph$) both by itself and in solution in a non-ionising solvent, such as pyridine, at a temperature above its decomposition point (87—88°). In the former case a minute quantity of the azoimide was obtained, probably owing to the action of the alkali of the glass or a trace of moisture or both, but none of it was formed in the latter experiment.

It is therefore evident that the ionic interpretation offers a plausible explanation of the reaction.

The reaction of the diazo-sulphonamide with an acid hydrolytic agent, *forming only* $R{\cdot}SO_2{\cdot}NH_2$ *and* $R'OH$ *but no* $R'NH_2$, *is* consistent with formula (II), because, of the two possible tautomeric forms, (II) and $R{\cdot}SO_2{\cdot}N{:}N{\cdot}NHR'$, the proximity of the positive charge on the sulphur should favour the stability of the ion (III) owing to its tendency to neutralise the negative charge on the nearest nitrogen atom. The two lone pairs of electrons on this *nitrogen* would then appropriate two hydrogen ions, completing the system $R{\cdot}SO_2{\cdot}NH_2$ *and leaving a positive ion,* $R'{-}N{\equiv}N$, which is responsible for the formation of the phenol. In this instance, therefore, the electronic condition is such that the substance ceases to be tautomeric.

The action of acid hydrolytic agents fails to distinguish, as Forster and Garland *have pointed out* (*J.*, 1909, **95**, 2056), between the tautomeric forms of an aromatic diazoamine, although phenyl-α-naphthyltriazene (Dimroth, Elbe, and Gruhl, *Ber.*, 1907, **40**, 2390) may have the constitution $NHPh{\cdot}N{:}N{\cdot}C_{10}H_7$, because it yields only aniline and no α-naphthylamine when hydrolysed by means of hydrochloric acid *in a freezing mixture.*

Further, the diazo-sulphonamide is readily methylated in the cold, forming only one monomethyl derivative which, from the evidence

of its reduction products ($R{\cdot}SO_2{\cdot}NH_2$, NH_3, $R'{\cdot}NHMe$, $R'NMe{\cdot}NH_2$, and $R'MeN{\cdot}N{:}N{\cdot}NMeR'$), must be regarded as having the constitution $R{\cdot}SO_2{\cdot}N{:}N{\cdot}NMeR'$ (V). The electronic hypothesis in our opinion offers an explanation of this behaviour. Obviously the methyl derivative cannot have been formed by direct substitution because of the greater stability of the form (II), which should have given the isomeride, $R{\cdot}SO_2{\cdot}NMe{\cdot}N{:}NR'$, and consequently its formation must have been preceded by salt formation with CH_3X at one of the nitrogen atoms. The velocity of methylation is much greater than that of the reaction (I); in other words, *it is the* substance (II), and not the ion (III), that takes part in this reaction. Now the electron pull due to the positive charges should influence all the nitrogen atoms in the chain, but the farthest one should have its lone pair of electrons comparatively free to take part in any salt formation. *This should lead to the formation of the complex* (IV), which would subsequently eliminate HX and form (V).

$$\text{(IV.)}\ [R{\cdot}SO_2{-}NH{-}N{=}\overset{CH_3}{\overset{|+}{N}}{-}R']\bar{X} \longrightarrow R{\cdot}SO_2{-}\bar{N}{-}N{=}\overset{CH_3}{\overset{|+}{N}}{-}R' \longrightarrow$$

$$R{\cdot}SO_2{-}N{=}N{-}N(CH_3){\cdot}R'\ \text{(V.)}$$

The isomeric methyl derivative, $R{\cdot}SO_2{\cdot}NMe{\cdot}N{:}NR'$, prepared from $R{\cdot}SO_2{\cdot}NHMe$ and $R'{\cdot}N_2Cl$, on reduction yields products ($R'NH_2$ and $R'NH{\cdot}NH_2$) which indicate that it is distinct from the substance (V).

In contrast with the formation of the monomethyl derivative of the diazo-sulphonamide, attention may be directed to the examples containing the system $\cdot CO{\cdot}\overset{|}{C}H{\cdot}N{:}N{\cdot}R$ described by Auwers (*Annalen*, 1911, **378**, 242), which on direct methylation yield two monomethyl derivatives, one an *O*-methyl and the other an *N*-methyl (next to the group R) derivative. In our opinion this difference is due to the fact that the diazo-sulphonamides do not possess the unsaturated centres that are necessary for enolisation previous to *O*-methylation.

EXPERIMENTAL.

Action of Heat on Benzenesulphon-p-tolyldiazoamide (II; R = Ph, $R' = C_7H_7$).—The diazo-sulphonamide (10 g., purified as previously described and dried in a vacuum desiccator over phosphoric oxide during several weeks) was heated in a vacuum. At about 80°, slow decomposition took place, producing much tar, and a few drops of an oily liquid distilled which smelt strongly of phenylazoimide (identified in the usual way). It is not advisable to use more of the diazo-sulphonamide for each experiment or heat it to a much higher temperature, as it is liable to explode.

The diazo-sulphonamide dissolves readily in cold pyridine and is precipitated unchanged on addition of water. The pure material (5 g.) was dissolved in 50 c.c. of pyridine and heated on the steam-bath for 12—15 hours; the solution was then cooled and poured into sufficient ice-cold dilute sulphuric acid (about 2%) to give an acid solution. Some resinous product separated, but no phenylazoimide.

Action of Glacial Acetic Acid on the Diazo-sulphonamide.—The crude substance (10 g., prepared in very dilute alkaline solution and precipitated by acetic acid) was treated with about 50 c.c. of glacial acetic acid, slowly warmed a few degreesabove the ordinary temperature, and occasionally stirred. It dissolved readily, the colour of the solution, at first light red, gradually darkened, and slow decomposition took place with evolution of gas. From the mixture, diluted with a large volume of water and made alkaline, ether extracted a trace of tar but no aniline. The aqueous solution was acidified and distilled in steam, and phenol identified in the distillate. The residue on cooling gave crystals of *p*-toluenesulphonamide (identified by mixed melting point).

Methylation of the Diazo-sulphonamide.—A solution of 51 g. of *p*-toluenesulphonamide in 3 l. of 2% aqueous sodium hydroxide cooled in ice and salt, was treated with a diazo-solution (made fron 28 g. of aniline dissolved in 90 c.c. of concentrated hydrochloric aci and 120 c.c. of water and diazotised with 22 g. of sodium nitrit dissolved in 70 c.c. of water). To the clear alkaline solution of th diazo-sulphonamide, 80 g. of methyl sulphate were added durin one hour, and the agitation continued for 3—4 hours longer. Th reddish-brown amorphous mass that separated was collecte washed, and dried in a vacuum desiccator; m. p. 115—118° (decomp. yield about 75 g. It smelt strongly of phenylazoimide.* Aft crystallising twice from methyl alcohol (animal charcoal), it wa obtained in colourless prismatic needles, m. p. 124—125° (decomp (Found: S, 10·9; N, 14·7. $C_{14}H_{15}O_2N_3S$ requires S, 11·1; N, 14·5%

Reduction of the Methyl Derivative (V).—A suspension of 20 g. the pure methyl derivative in 300 c.c. of methyl alcohol was reduc with 600 g. of sodium amalgam (2½%). The evolution of ammon was soon noticed, and as the reaction progressed the ether dissolv and finally a small amount of a crystalline substance separate The whole mixture was then distilled in steam. The residue in t distilling flask, which contained the crystals (A) referred to abo was filtered off and well washed with water. The filtrate,

* When the diazo-sulphonamide itself is stirred even for much lon periods with alkali of the strength used in this experiment, very little of azoimide is formed, showing that the methylation proceeds at a much fa rate.

acidification with hydrochloric acid, gave a colourless solid which was identified as *p*-toluenesulphonamide (mixed m. p.) after recrystallisation. The presence of *p*-toluenesulphonmethylamide could not be detected in this product.

The crystalline residue (A) on recrystallisation from spirit (animal charcoal) separated in almost colourless plates, m. p. 141—142° (decomp.), and proved to be identical with diphenyldimethyltetrazene, NPhMe·N:N·NMePh, prepared by oxidising αα-phenylmethylhydrazine in chloroform solution by means of mercuric oxide (Fisher, *Annalen*, 1877, **190**, 167; Tafel. *Ber.*, 1885, **18**, 1744). The melting point observed by us was, however, 4° higher than that recorded in the literature.

The steam-distillate from the original reduction mixture was acidified with hydrochloric acid and evaporated to dryness. From the dark brown residue (B), hot chloroform extracted monomethylaniline, which was isolated and identified in the form of the hydrochloride, m. p. 125—126° (the material obtained from several experiments was sufficient for the preparation of the acetyl derivative). No other basic substance could be detected in the chloroform extract.

The portion of the residue (B) insoluble in chloroform was extracted with absolute alcohol, which left behind crystals of ammonium chloride. The extracts of the residue from several experiments were collected together and the base was liberated by means of alkali, extracted with ether, dried, and distilled in a vacuum. The pale yellow, oily liquid, b. p. 160°/70 mm., gave an acetyl derivative in hexagonal prisms, m. p. 92—93°, and a crystalline hydrochloride, m. p. 221—222° (decomp.), both identical with those obtained from an authentic specimen of *as*-phenylmethylhydrazine. No trace of methylamine hydrochloride could be detected in the residue insoluble in chloroform.

Action of Benzenediazonium Chloride on p-*Toluenesulphonmethylamide*.—A solution of 5 g. of the methyl ether in dilute aqueous sodium hydroxide was treated in the cold with the diazo-solution made from 5 g. of aniline. The reaction was very slow and a brownish-red viscous mass gradually separated. As this did not show any sign of solidifying, it was washed several times by trituration with water. The gummy residue was soluble in most organic solvents but did not crystallise from any of them.

When its alcoholic solution was reduced by means of sodium amalgam as before, the evolution of ammonia was soon noticed. The mixture after reduction was poured into excess of water and extracted with ether. The ethereal extract on evaporation gave a dark oil, soluble in dilute acids, which was apparently a mixture of

aniline and phenylhydrazine, as it gave the carbylamine reaction, and phenylazoimide and phenol on treatment with nitrous acid. No *trace of methylaniline could be detected in the residue.*

One of the authors (P.K.D.) desires to thank the Research Fund Committee of the Chemical Society for a grant which has defrayed most of the cost of this investigation.

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CCLXV.—*The Decomposition of Acetyl Peroxide and the Mechanism of Kolbe's Electrosynthesis.*

By OSWALD JAMES WALKER.

THE earlier idea of Schall (*Z. Elektrochem.*, 1896, **3**, 83), that acid peroxides are formed as intermediate products at the anode during the electrolysis of fatty acids, has in recent years been taken up by Fichter (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 131; *J. Chim. phys.*, 1926, **23**, 493), who has extended the peroxide theory to electrochemical oxidation in general. It is the purpose of this paper to show that the experimental justification for this view is unsound and that there is no necessity to assume that acetyl peroxide is formed during the electrolysis of acetates.

Whatever view we adopt regarding the mechanism of Kolbe's reaction we must assume that free $CH_3\cdot CO\cdot O$ radicals are present at some stage in the process. If we accept the discharged-ion theory, *i.e.*, that the $CH_3\cdot CO\cdot O$ radicals result simply from the discharge of acetanions and not from a dehydration of acetic acid by oxygen (compare Fairweather and Walker, J., 1926, 3111 *), the question still arises: Do the $CH_3\cdot CO\cdot O$ radicals unite to form acetyl peroxide which then decomposes into carbon dioxide and ethane; or do they decompose "unimolecularly," so to speak, into carbon dioxide and free CH_3 radicals, which then unite to form ethane?

The first view may be tested, as Fichter suggested, by preparing the pure acetyl peroxide and causing it to decompose. The application of results of such experiments to the Kolbe reaction at the anode may, however, not be conclusive. For even assuming that acetyl peroxide decomposes on heating entirely into carbon dioxide and ethane, it does not follow that in the anode process, in which

* The values of the anode potential in that paper are through a regrettable error in the calculation all 0·56 volt too high. This in no way affects the reasoning in the paper, which is concerned only with the relative values of the potentials.

these gases are obtained from discharged acetanions, the $CH_3{\cdot}CO{\cdot}O$ radicals must have first united to form a peroxide. On the contrary, one may argue that acetyl peroxide, when heated, breaks up into two $CH_3{\cdot}CO{\cdot}O$ groups, which then react as in the electrical process (compare Wieland and Fischer, *Annalen*, 1925, **446**, 60). It will be seen, however, from the experimental part that a simple decomposition of acetyl peroxide according to the equation $(CH_3{\cdot}CO{\cdot}O{\cdot})_2 = C_2H_6 + 2CO_2$ does not take place.

Fichter (*Helv. Chim. Acta*, 1927, **10**, 869) claims to have obtained direct evidence for the peroxide theory, since he has shown that in the electrolysis of a solution of potassium hexoate small quantities of hexoyl peroxide are formed when the temperature is kept very low. This experiment shows that when the conditions are made very favourable the discharged acyl radicals unite to a small extent to form the acid peroxide, but one is not justified in concluding that the Kolbe synthesis, which is the main reaction, has proceeded through the intermediate stage of peroxide. In fact, the difficulty of isolating from the electrochemical products any peroxide at temperatures at which these peroxides are by no means unstable cannot be reconciled with this view. A further difficulty arises when one considers that by electrolysing a solution of an acetate at about 100° considerable quantities of ethane are obtained, although acetyl peroxide decomposes well below this temperature (see experimental part). Also Gibson (*Proc. Roy. Soc. Edin.*, 1924, **44**, 151) has shown that hexachloroethane is formed in the electrolysis of trichloroacetic acid, of which the peroxide is apparently incapable of existence.

The decomposition of acetyl peroxide, on which Fichter largely bases his theory, has really not been studied to any extent (for the previous literature on the subject, see Fichter, *Helv. Chim. Acta*, 1918, **1**, 151). It was decided, therefore, to investigate the nature and composition of the gases obtained by the decomposition of acetyl peroxide under various conditions.

EXPERIMENTAL.

Acetyl peroxide was prepared from acetic anhydride and sodium peroxide by the method of Gambarjan (*Ber.*, 1909, **42**, 4010). The ethereal solution of peroxide was dried over calcium chloride, the ether evaporated at the ordinary temperature, and the crystalline residue of peroxide washed with ether; it was then sufficiently pure, m. p. 26·5° (Nef gives 30°, and Colson 27°). Analysis: A mixture of 0·1—0·2 g. of the peroxide, 50 c.c. of water, 10 c.c. of glacial acetic acid, and 10 c.c. of a 20% solution of potassium iodide was kept for 24 hours (the liberation of iodine takes place slowly;

compare Clover and Richmond, *Amer. Chem. J.*, 1903, **29**, 183) and the iodine was then titrated with $N/10$-thiosulphate. Independently prepared samples of the peroxide were found to contain 99·6, 99·8, and 99·4% of $(CH_3{\cdot}CO{\cdot}O{\cdot})_2$.

In all the experiments that follow, the gases evolved were collected over mercury and analysed in the usual manner in a Bone and Wheeler apparatus containing mercury.

Decomposition of Pure Acetyl Peroxide.—When acetyl peroxide is heated gradually above its melting point the liquid commences to evolve gas at 60—70°, and at 80° the evolution proceeds briskly. The decomposition takes place gently without the violent explosion that occurs when the substance is heated rapidly. The composition of the gas (% vol.) evolved at 80° is: CO_2, 58·7, 61·0; C_2H_4, 1·1, 1·6; O_2, —, 2·3; CO, 1·6, 3·0; CH_4, 34·0, 28·8; C_2H_6, 4·6, 3·4.

The proportion of methane formed is greater than in the explosive decomposition of acetyl peroxide investigated by Fichter (*Helv. Chim. Acta*, 1918, **1**, 152), which did not lead to a simple disintegration according to the equation $CH_3{\cdot}CO{\cdot}O{\cdot}O{\cdot}OC{\cdot}CH_3 = C_2H_6 + 2CO_2$. He also found considerable quantities of methane and ascribed its formation to a sort of "cracking" process, due to the violence of the explosion and the high temperature of the decomposition, which he supposes does not occur in the slow molecule-by-molecule decomposition at the anode.

A further experiment, in which the decomposition was carried out quantitatively and as slowly as possible, showed that the absolute yield of ethane, calculated on the weight of peroxide used, is very small. In a small, weighed tube 0·0500 g. of acetyl peroxide was gently heated till decomposition commenced at 61°. The heating was continued, at 65—75°, for about 4 hours, 11·0 c.c. of gas (measured at 13° and 754 mm.) being collected. The residue weighed 0·0257 g., and the amount of undecomposed peroxide in it, estimated by liberation of iodine from potassium iodide, was 0·017[illegible] g. The decomposed peroxide (0·0330 g.) therefore produce[illegible] 10·4 c.c. of gas (reduced to N.T.P.) having the following percentag[illegible] composition by volume: CO_2, 58·3; O_2, 0·2; CO, 0·9; CH_4, 38·6 C_2H_6, 1·9. This corresponds to 1·0 molecule of carbon dioxid[illegible] 0·65 molecule of methane, and 0·04 molecule of ethane from molecule of peroxide. The formation of ethane is therefore certain[illegible] not the main reaction.

Decomposition of Solutions of Acetyl Peroxide.—When a solutio[illegible] (100 g.) of acetyl peroxide (14·4 g.) in water containing acetic ac[illegible] (27·7 g., to increase the solubility) was gradually warmed, efferve[illegible] cence set in at about 75° and between 80° and 90° there was a bri[illegible]

evolution of gas. The gases evolved at about 80° were collected and analysed (expts. *a* and *b*).

Acetyl peroxide dissolved in	CO_2.	C_2H_4.	O_2.	CO.	CH_4.	C_2H_6.
a. Aqueous acetic acid	76·0	1·2	3·1	1·4	16·0	2·3
b. " "	75·0	—	1·4	1·4	20·8	1·2
c. Ethyl alcohol	50·5	—	—	2·2	45·8	1·5
d. " "	51·0	—	—	1·7	45·6	1·7

Here again the amount of ethane formed is small compared with that of methane and there is relatively more carbon dioxide.

A solution of 0·15 g. of acetyl peroxide in 0·4 c.c. of alcohol was heated gradually in a water-bath. Gas evolution commenced at about 60°. The gas evolved between 60° and 70° was collected after passing through a cooled tube to condense any alcohol vapour; it consisted mainly of carbon dioxide and methane in nearly equal volumes, with only a very small amount of ethane (see expts. *c* and *d* in the table).

From these experiments, it is evident that the decomposition of acetyl peroxide does not take place to any large extent according to the equation $(CH_3{\cdot}CO{\cdot}O{\cdot})_2 = C_2H_6 + 2CO_2$, and hence there is no reason to suppose that in the electrolysis of acetates, where the gases evolved at the anode are essentially carhon dioxide and ethane, acetyl peroxide has been formed at the anode. It must also he emphasised that methane is not present in the anode gases, although it appears to be one of the necessary products in the decomposition of acetyl peroxide. The only electrolytic formation of methane from acetates is recorded by Baur (*Z. Elektrochem.*, 1923, **29**, 105), who used commutated direct current.

There is the possibility that the methane obtained in the above experiments from aqueous solutions of acetyl peroxide may have come from decomposition not of the peroxide itself but of the peracid which is got from it by hydrolysis. It has been shown by Clover and Richmond (*loc. cit.*, p. 184) that a solution of acetyl peroxide kept for 24 hours undergoes the change:

$$CH_3{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}CH_3 + H_2O = CH_3{\cdot}CO{\cdot}O{\cdot}OH + CH_3{\cdot}CO{\cdot}OH.$$

A solution of the peroxide which had been kept for a week liberated almost the whole of the required amount of iodine immediately after the addition of potassium iodide, showing that the change from peroxide to peracid was practically complete (since the former liberates iodine only very slowly). The solution of peracid was heated gradually and at about 40° gas evolution commenced. The gas evolved between 75° and 80° consisted mainly of oxygen with about 10% of carbon dioxide and no trace of ethane or methane. Hence the decomposition of the peroxide does not proceed through the peracid stage.

In the search for a method whereby acetyl peroxide might be decomposed at lower temperatures than those employed so far, the action of ultra-violet light on the peroxide was investigated: the peroxide decomposed, and larger quantities of ethane were obtained than by any of the previous methods. A solution of acetyl peroxide in aqueous acetic acid was placed in a quartz tube surrounded by a water-cooled quartz condenser and was exposed at a distance of 3 or 4 inches to the light of a mercury vapour lamp. A gas was slowly evolved and after 7 or 8 hours about 5 c.c. had collected. The composition of the gas is shown in the table (expts. *a* and *b*).

Acetyl peroxide.	CO_2.	C_2H_4.	O_2.	CO.	CH_4.	C_2H_6.
a. Dissolved in aqueous acetic acid	75·4	—	1·2	1·4	4·8	17·3
b. ,, ,, ,, ,,	68·5	—	1·4	1·3	11·8	17·1
c. Solid	66·8	—	1·3	1·2	5·6	25·1
d. ,,	68·4	2·1	0·7	1·3	3·9	23·6
e. ,,	67·4	2·0	0·5	1·4	4·4	24·4

In experiments *c*, *d*, and *e*, solid acetyl peroxide was exposed to the ultra-violet light for about 3 hours. The amount of ethane formed was much greater than in the thermal decomposition. Even in this case, however, there is no reason to suppose that the main reaction consists in a simple breaking up of the acetyl peroxide into ethane and carbon dioxide.

Conclusion.

The results of the experiments described in this paper make it appear extremely unlikely that the formation of ethane and carbon dioxide at the anode in the electrolysis of acetates proceeds through the intermediate stage of acetyl peroxide. The view that the discharged acetate ions, which must necessarily be very unstable radicals, react together to give the above-mentioned products still affords the most satisfactory, although perhaps incomplete explanation of Kolbe's electrosynthesis. In the interaction of these radicals some sort of momentary loose union may well take place prior to a more far-going disruption, but the assumption of the actual formation of the chemically known peroxide is unnecessary and also experimentally unsound. That a small portion of the acetate radicals might unite to form the more stable peroxide would not be surprising, and this possibility is not excluded.

The main arguments against the peroxide theory may be summed up as follows:

(1) The thermal decomposition of acetyl peroxide, both in the pure state and in solution, does not indicate a reaction according to the equation $(CH_3{\cdot}CO{\cdot}O)_2 = C_2H_6 + 2CO_2$.

(2) Methane, which is not found in the anode gases during t

electrolysis of acetates, is always present among the decomposition products of acetyl peroxide, often in large amounts.

(3) Peroxides have not as yet been isolated by electrochemical means, even at low temperatures at which the peroxides are comparatively stable.

I should like to thank Professor Sir James Walker, F.R.S., for his helpful advice during the course of this work.

UNIVERSITY OF EDINBURGH. [*Received, May 21st*, 1928.]

CCLXVI.—*The Adsorption of Vapours on an Amalgamated Platinum Surface.*

By JOHN WILLIAM SMITH.

THE *following experiments are a continuation of those of* McHaffie and Lenher (J., 1925, **127**, 1559) and of Lenher (J., 1926, 1785; 1927, 272), who studied the adsorption of water and of benzene vapours on glass, silica, and platinum surfaces at temperatures near the saturation temperature. Assuming the surface to be perfectly plane, they deduced that this adsorption was multimolecular. This hypothesis, however, has been criticised by Fraser, Patrick, and Smith (*J. Physical Chem.*, 1927, **31**, 897) on the ground that the walls of the adsorption vessels employed were not plane, as they had been etched by acid cleaning. This was supported by the observation that the effect was not present in the case of toluene vapour on a freshly-blown glass surface which had not been exposed to moisture. The work here recorded was commenced in the belief that amalgamation of the platinum vessel would produce a perfectly plane surface without the possibility of capillaries in which the adsorbing gas could condense.

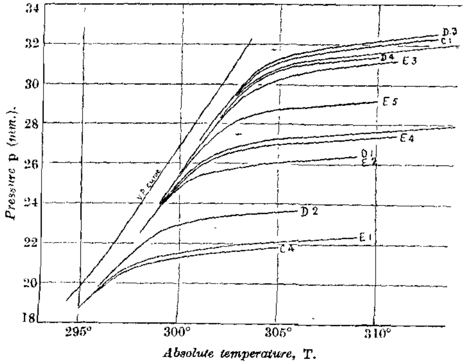
EXPERIMENTAL.

The Adsorption of Water Vapour on an Amalgamated Platinum Surface.—The apparatus employed was exactly the type used by McHaffie and Lenher (*loc. cit.*). The platinum vessel, together with a short length of glass tubing, was removed from the U-tube. It was filled with freshly prepared sodium amalgam, the end closed, and the bulb allowed to stand over-night. The amalgam was then removed, and the inside of the vessel washed repeatedly with clean dry mercury. The last traces of the sodium were finally removed by repeated washing with water. The vessel was then replaced in position, care being taken not to heat the platinum vessel and thereby drive off the mercury from its surface. Blowing was

performed through a long tube packed with phosphoric oxide a glass wool so as to prevent the admission of grease. Experime were then carried out in the manner described by McHaffie a Lenher.

The amalgamated surface was perfectly reproducible, but no case could a normal vapour-pressure curve be obtained in amalgamated vessel. The same curve was always reached at lower temperatures, *viz.*, about 1·3 mm. below the normal vap pressure. This value was remarkably constant over the temperat range investigated. After thorough cleaning and reamalgama of the surface, the same curve was always obtained. In each

Fig. 1.



the vessel was very thoroughly washed for some time aft washings had lost all trace of alkaline reaction. In one after a series of readings had been taken, the bulb was discon and again washed about 50 times with water, but exactly th effect was observed. A selection of the results obtained is in Table I; T is the absolute temperature, and p the p (mm. of mercury at 0°) read at the corresponding tempe The volume of the platinum bulb was 5·317 c.c. and its i surface area 15·36 sq. cm.

In Fig. 1, the values of T are plotted as abscissæ against th sponding pressures p as ordinates. The vapour-pressure c water is also given, plotted from the data of Scheel and

TABLE I.

T.	p.	N/cm.² $\times 10^{-14}$.	θ.	T.	p.	N/cm.² $\times 10^{-14}$.	θ.
	Expt. No. D.3.				Expt. No. E.3.		
313°	32·51	—	—	311	31·20	—	—
310	32·20	—	—	307	30·76	—	—
308	31·90	9·5	0·8	305	30·23	39·3	3·3
306	31·55	23·8	2·0	304	29·79	77·3	6·5
305	31·22	50·0	4·2	303	29·25	127·3	10·7
304	30·71	94·0	7·9	302	28·30	220·1	18·5
303	29·80	184·4	15·5	301	27·00	353·4	29·7
302	28·57	309·4	26·0	300	26·67	496·2	41·7
	Expt. No. E.2.				Expt. No. E.5.		
309	26·40	—	—	310	29·19	—	—
306	26·15	—	—	307	28·92	—	—
304	25·97	—	—	305	28·72	—	—
303	25·82	9·5	0·8	304	28·56	9·5	0·8
302	25·65	20·2	1·7	303	28·20	36·9	3·1
301	25·39	40·5	3·4	302	27·58	97·6	8·2
300	24·75	100·0	8·4	301	26·67	188·0	15·8
299	23·70	186·8	15·7	300	25·40	322·5	27·1
298	22·50	335·6	28·2	299	24·00	477·2	40·1
	Expt. No. C.2.				Expt. No. C.4.		
313	27·85	—	—	305	21·83	—	—
310	27·61	—	—	303	21·63	—	—
307	27·38	—	—	301	21·42	—	—
305	27·20	—	—	300	21·31	16·7	1·4
303	26·87	20·2	1·7	299	21·10	33·3	2·8
302	26·50	50·0	4·2	298	20·83	55·9	4·7
301	26·00	96·4	8·1	297	20·46	90·4	7·6
300	25·09	188·0	15·8	296	19·75	173·7	14·6
299	23·94	308·2	25·9	295	18·70	268·9	22·6
298	22·50	453·4	38·1	294	17·60	386·7	32·5
			Expt. No. D.2.				
306	23·67	—	—	300	22·91	29·7	2·5
305	23·58	—	—	299	22·60	53·5	4·5
304	23·50	—	—	298	21·87	114·2	9·6
303	23·41	—	—	297	20·97	221·3	18·6
302	23·31	—	—	296	19·87	339·1	28·5
301	23·18	6·7	0·56				

(*Ann. Physik*, 1910, **31**, 715). The series letters C, D, and E refer to different amalgamated surfaces. Between each series the surface was cleaned with nitric acid, washed, and reamalgamated as described above. This treatment did not alter the nature of the platinum surface itself, for the same adsorption curves were obtained before and after treatment.

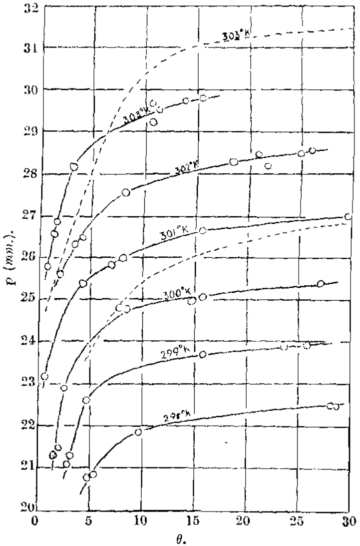
As in the case of McHaffie and Lenher's experiments, the number of molecules adsorbed per sq. cm. (N/cm.²) is given by

$$N/\text{cm.}^2 = (p/T - p_1/T_1) \times 3{\cdot}359 \times 10^{18},$$

where p is the pressure at some point on the linear portion of the

experimental curve at the temperature T, and p_1 and T_1 are the *corresponding values for the point* under consideration. The constant $3{\cdot}359 \times 10^{18}$ is calculated from the dimensions of the platinum vessel. Similarly, the number of molecular layers adsorbed is given by $\theta = (p/T - p_1/T_1) \times 2824$.

FIG. 2.



In *Fig.* 2, the thickness θ of the adsorbed film is plotted against p, the equilibrium pressure of the film at constant temperature. Small pressure differences become greatly magnified when plotted in this way, and the fact that the results at any one temperature of all three series lie on the same smooth curve attests to the constant nature of the surface. For comparison, two of the isotherms found by McHaffie and Lenher for a platinum surface are also included as broken lines.

The Adsorption of Benzene Vapour on an Amalgamated Platinum Surface.—The adsorption vessel was amalgamated in exactly the same manner as for the previous series of experiments, but in some cases the surface was washed only with dry mercury, whilst in the others it was also washed repeatedly with water. Both surfaces gave the same type of curve, but that washed with water gave the more consistent results. A few of the results obtained with such water-washed surfaces are in Table II.

TABLE II.

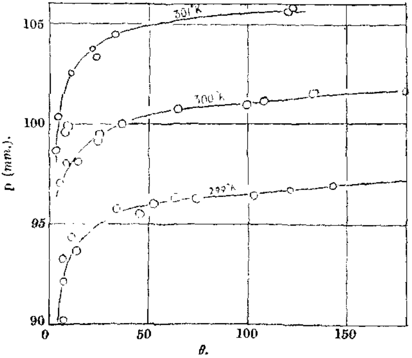
T.	*p.*	*N*/cm.^{2} $\times 10^{-14}$.	*θ.*	*T.*	*p.*	*N*/cm.^{2} $\times 10^{-14}$.	*θ.*
	Expt. No. L.1.				Expt. No. L. 2.		
307·0°	110·90	—	—	307·0°	107·49	—	—
306·0	110·53	—	—	306·0	107·15	—	—
305·0	110·16	—	—	305·0	106·84	—	—
304·0	109·79	—	—	304·0	106·41	—	—
303·5	109·62	—	—	303·0	105·95	10·0	3·5
303·0	109·34	13·5	4·7	302·5	105·72	16·6	5·8
302·6	109·05	27·0	9·4	302·0	105·45	26·7	9·3
302·2	108·68	53·7	18·7	301·8	105·29	37·0	12·9
302·0	108·40	77·2	26·9	301·6	105·15	47·1	16·4
301·8	108·10	100·7	35·1	301·4	105·00	53·7	18·7
301·6	107·53	157·9	55·0	301·2	104·79	70·6	24·6
301·4	106·93	215·2	75·0	301·0	104·51	94·1	32·8
301·2	106·43	265·2	92·4	300·8	104·12	130·9	45·6
301·0	105·63	345·8	120·5	300·6	103·62	177·9	62·0
300·8	104·87	423·0	147·4	300·4	102·97	250·0	87·1
300·6	104·04	507·1	176·7	300·2	102·25	315·7	110·0
300·0	101·64	750·2	261·4	300·0	101·57	382·9	133·4
299·7	100·25	896·6	312·4	299·8	100·79	463·5	161·6
				299·6	99·91	553·9	193·0
				299·2	98·08	745·3	259·7
				299·0	97·27	858·1	299·0
	Expt. No. M.7.				Expt. No. M.9.		
304·0	91·79	—	—	306·0	103·54	—	—
303·0	91·47	—	—	305·0	103·24	—	—
302·0	91·17	—	—	304·0	102·92	—	—
301·0	90·85	—	—	303·0	102·60	—	—
300·0	90·52	3·4	1·2	302·0	102·18	—	—
299·0	90·10	16·6	5·8	301·2	101·71	27·0	9·4
298·4	89·82	27·0	9·4	301·0	101·58	33·6	11·7
298·2	89·66	40·2	14·0	300·8	101·41	43·6	15·2
298·0	89·54	47·1	16·4	300·6	101·23	57·1	19·9
297·8	89·27	70·6	24·6	300·4	100·98	77·2	26·9
297·6	88·98	97·3	33·9	300·2	100·71	100·7	35·1
297·4	88·65	127·7	44·5	300·0	100·40	127·7	44·5
297·2	88·21	167·9	58·5	299·8	99·90	174·5	60·8
297·0	87·71	221·6	77·2	299·6	99·31	235·1	81·9
296·8	87·22	268·6	93·6	299·4	98·63	302·2	105·3
296·6	86·65	325·7	113·5	299·2	97·66	393·0	140·4
296·4	86·03	389·5	135·7	299·0	96·85	486·8	169·6
296·2	85·34	460·1	160·3				
296·0	84·64	533·8	186·0				

TABLE II (*contd.*).

T.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.	T.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.
	Expt. No. L.9.				Expt. No. J.3.		
306·0	100·47	—	—	304·0	95·37	—	—
305·0	100·13	—	—	303·0	95·00	—	—
304·0	99·80	—	—	302·0	94·62	—	—
303·0	99·46	—	—	301·0	94·24	—	—
302·0	99·13	—	—	300·0	93·84	—	—
301·5	98·92	—	—	299·8	93·76	—	—
301·0	98·69	10·0	3·5	299·6	93·68	—	—
300·6	98·52	16·6	5·8	299·4	93·60	—	—
300·4	98·44	20·1	7·0	299·2	93·48	6·6	2·3
300·2	98·29	27·0	9·4	299·0	93·33	16·6	5·8
300·0	98·11	40·2	14·0	298·8	93·16	27·0	9·4
299·8	97·88	57·1	19·9	298·6	92·89	50·2	17·5
299·6	97·60	80·6	28·1	298·4	92·60	77·2	26·9
299·4	97·23	117·4	40·9	298·2	92·29	104·2	36·3
299·2	96·79	157·8	55·0	298·0	91·82	151·0	52·6
299·0	96·26	211·5	73·7	297·8	91·30	201·5	70·2
298·8	95·73	265·2	92·4	297·6	90·70	262·0	91·3
298·6	95·03	335·5	116·9	297·4	90·08	325·7	113·5
298·4	94·31	409·5	142·7	297·2	89·45	389·5	135·7
298·2	93·71	470·1	163·8	297·0	88·73	463·5	161·5

The number of molecules adsorbed per sq. cm. is given by the same formula as before, and θ is given by $\theta = (p/T - p_1/T_1) \times 1{\cdot}169 \times 10^4$ (Lenher, J., 1927, 276).

FIG. 3.



The adsorption isotherms for a few temperatures are plotted in Fig. 3. In this case, again, the remarkable effect was observed

that the vapour pressure obtained was about 1·6 mm. below the normal value. This was confirmed by introducing benzene till it formed a definite meniscus above the mercury, and then determining the vapour-pressure curve. This followed exactly the curve traced by the lower portions of the other pressure–temperature curves.

Summary.

1. The adsorption of water vapour and of benzene vapour on an amalgamated platinum surface at pressures near the saturation values has been studied.

2. Such a surface is quite permanent in both vapours, but not in the laboratory atmosphere.

3. Both cases show definite effects of the type found by McHaffie and Lenher, and thus support their view that under such conditions multimolecular adsorbed films are produced, in spite of the fact that the surface, being virtually a liquid mercury surface, is presumably incapable of containing capillary cavities of the type postulated by Fraser, Patrick, and Smith.

4. In the amalgamated vessel the vapour pressure of the liquids was always low—to the extent of 1·3 mm. in the case of water and 1·6 mm. with benzene. This was constant throughout the temperature range investigated.

In conclusion, the author desires to express his great indebtedness to the Department of Scientific and Industrial Research for a grant during the tenure of which this research was carried out, and especially to Professor F. G. Donnan, F.R.S., at whose suggestion this work was undertaken, for his kindly advice and criticism during its progress.

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CCLXVII.—*Halogen Derivatives of* o- *and* p-*Azophenol.*

By LOUIS HUNTER and RONALD SIDNEY BARNES.

PREVIOUS attempts to obtain halogen derivatives of *o*- and *p*-azophenol (2 : 2′- and 4 : 4′-dihydroxyazobenzene) have resulted in the isolation of the tetrabromo-compounds (Weselsky and Benedikt, *Annalen*, 1879, **196**, 340) and of a trichloro-*o*-azophenol (Bohn and Heumann, *Ber.*, 1882, **15**, 1499). That the direct action of elementary halogens on these phenols is not entirely one of simple

substitution is shown by the fact that the latter authors isolated only *s*-trichlorophenol from the action of chlorine upon *p*-azophenol.

The present investigation was originally undertaken with a view to obtaining some of the higher chloro-derivatives of the azophenols, and later as a means of preparation of some substituted aminophenols. So well did these azophenols lend themselves to progressive halogenation that, with the exception of tribromo- and tri-iodo-*o*-azophenol, all the anticipated stages from the mono- to the tetra-halogen substitution products have been obtained, *viz.*, those possessing substituent halogen in positions ortho and para to the hydroxyl groups, although all the possible isomerides were not isolated. The chloroamine method of halogenation (Orton and King J., 1911, **99**, 1185) was used throughout this investigation, toluene-*p* sulphondichloroamide ("dichloramine-T") being employed (Bradfield Cooper, and Orton, J., 1927, 2854; Bradfield, Orton, and Roberts this vol., p. 782). The bromo-compounds described are the first to b prepared by the chloroamine method, thus bringing bromination int line with chlorination and iodination in this respect. The result amply illustrate the extreme delicacy of the chloroamine methoc

The positions taken up in the azophenol molecules by the sub stituent halogen atoms were readily determined by reduction to th corresponding aminophenols, and it was thus found that *p*-azo phenol yielded only the 3 : 3′- and not the 3 : 5-dihalogen derivative on dihalogenation, and that in the mono-substitute *o*-azophenols the halogen atom occupied the 5-position apparentl to the exclusion of the 3-position.

Owing to its structure *p*-azophenol is more liable to oxidatic than its *o*-isomeride, and instead of substitution iodinating agen cause partial oxidation to a quinhydrone-like complex,

$$O{:}C_6H_4{:}N{\cdot}N{:}C_6H_4{:}O,HO{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH,$$

which on further oxidation is transformed into *p*-quinoneazir $O{:}C_6H_4{:}N{\cdot}N{:}C_6H_4{:}O$. Iodination of *p*-azophenol or of its deri atives by all the usual methods was unsuccessful, though *o*-azopher was iodinated normally.

The action of more than four equivalents of halogenating age led in the chlorination of *p*-azophenol to the production of comp chloroquinones of a type similar to *p*-quinoneazine which have r been further investigated, but in all other cases yielded the tet substituted compound.

EXPERIMENTAL.

o- and *p*-Azophenols were prepared by Willstätter's modificat (*Ber.*, **1906**, **39**, 3492) of Weselsky and Benedikt's method (*loc. c* As pointed out by Robertson (J., 1913, **103**, 1472), *p*-azoph

monohydrate obtained by this method is the *trans*-form; and the compounds described in the present work retain the *trans*-configuration, since tetra-substituted derivatives are readily obtained. Similar arguments apply to *o*-azophenol, although no second modification of this compound has yet been obtained.

In the following account the typical procedure is described in detail for a chlorination, a bromination, and an iodination; all other halogenations are similar unless special precautions are mentioned. In most preparations, and more particularly in iodinations, acetic acid stable to halogens (Orton and Bradfield, J., 1924, **125**, 960) was used as a solvent.

Derivatives of p-*Azophenol* (4 : 4'-*Dihydroxyazobenzene*).—3-*Chloro*-4 : 4'-*dihydroxyazobenzene*. *p*-Azophenol (1·5 g.) was dissolved in glacial acetic acid (600 c.c.) and mixed with a solution of dichloramine-T (0·82 g.) in acetic acid (30 c.c.). A few drops of dilute hydrochloric acid were added, and the mixture was kept in the dark for about ½ hour; chlorination was then complete as shown by the absence of free chlorine. Since dilution with 1 l. of water failed to precipitate the product, caustic soda was added until the mixture was almost neutral. The brown deposit formed was washed, dried, and crystallised from 20% aqueous alcohol, giving fine red granules (1·1 g.), m. p. 184° (Found: Cl, 14·7. $C_{12}H_9O_2N_2Cl$ requires Cl, 14·3%).

The constitution of the compound was fixed by reduction with stannous chloride and hydrochloric acid, and isolation of a mixture of aminophenols; moreover, on further chlorination the substance was transformed into 3 : 3'-dichloro-4 : 4'-dihydroxyazobenzene, the constitution of which has been proved.

3-*Chloro*-4 : 4'-*diacetoxyazobenzene* crystallised from alcohol in fine orange needles, m. p. 160—161°, and the *dibenzoyl* derivative in yellow needles, m. p. 158—159°.

3 : 3'-*Dichloro*-4 : 4'-*dihydroxyazobenzene* formed rust-red needles, m. p. 195°, from alcohol (Found: Cl, 24·7. $C_{12}H_8O_2N_2Cl_2$ requires Cl, 25·0%). Reduction with stannous chloride yielded *o*-chloro-*p*-aminophenol. The *diacetyl* derivative crystallised from alcohol in fine orange needles, m. p. 199°, and the *dibenzoyl* derivative from benzene in bright yellow needles, m. p. 226°.

3 : 5 : 3'-*Trichloro*-4 : 4'-*dihydroxyazobenzene* formed yellow-brown needles, m. p. 172°, from 50% aqueous alcohol (Found: Cl, 33·4. $C_{12}H_7O_2N_2Cl_3$ requires Cl, 33·5%). Reduction with stannous chloride and hydrochloric acid gave a mixture of the hydrochlorides of a mono- and a di-chloro-*p*-aminophenol, and on further chlorination the compound yielded 3 : 5 : 3' : 5'-tetrachloro-4 : 4'-dihydroxyazobenzene, of known constitution.

The *diacetyl* derivative crystallised from benzene in fine orange needles, m. p. 207—208°, and the *dibenzoyl* derivative in yellow prisms, m. p. 189°.

3 : 5 : 3′ : 5′-*Tetrachloro*-4 : 4′-*dihydroxyazobenzene* was isolated as the hexahydrate, which formed fine yellow needles, m. p. 225°, from aqueous acetic acid (Found : H_2O, 22·9. $C_{12}H_6O_2N_2Cl_4,6H_2O$ requires H_2O, 23·4%). The anhydrous substance had m. p. 240° (Found : Cl, 40·4. $C_{12}H_6O_2N_2Cl_4$ requires Cl, 40·3%). Its product of reduction was 2 : 6-dichloro-4-aminophenol, m. p. 165°. Its *diacetyl* derivative formed yellow needles, m. p. 240°, from alcohol, and the *dibenzoyl* derivative orange needles, m. p. 244°, from benzene.

3-*Bromo*-4 : 4′-*dihydroxyazobenzene*. A solution of *p*-azophenol (2 g.) in stable acetic acid (600 c.c.) was treated with a solution of the brominating agent prepared by mixing solutions of dichloramine-T (1·6 g.) in acetic acid (50 c.c.) and potassium bromide (1·5 g.) in water (20 c.c.). After 30 minutes no free bromine could be detected, and the product was precipitated by partly neutralising the acetic acid and diluting the mixture with water. The product crystallised from aqueous alcohol in yellow needles (2·6 g.), m. p. 153°, which rapidly darkened on exposure to light (Found : Br, 26·9. $C_{12}H_9O_2N_2Br$ requires Br, 27·3%).

Reduction afforded a mixture of *p*-aminophenol and its monobromo-compound, and the constitution of the azophenol was confirmed by further bromination, yielding 3 : 3′-dibromo-4 : 4′-dihydroxyazobenzene (see below).

3-*Bromo*-4 : 4′-*diacetoxyazobenzene* crystallised from benzene in orange needles, m. p. 142°, and the *dibenzoyl* derivative in yellow prisms, m. p. 165—166°.

3 : 3′-*Dibromo*-4 : 4′-*dihydroxyazobenzene* crystallised from alcohol in light brown needles, m. p. 175°, which darkened on exposure (Found : Br, 42·4. $C_{12}H_8O_2N_2Br_2$ requires Br, 43·0%). Reduction yielded *o*-bromo-*p*-aminophenol, m. p. 154°, thus confirming the constitution of the azophenol.

The *diacetyl* derivative crystallised from alcohol in yellow-orange needles, m. p. 161°, and the *dibenzoyl* derivative from benzene in pale yellow needles, m. p. 227°.

3 : 5 : 3′-*Tribromo*-4 : 4′-*dihydroxyazobenzene* crystallised from aqueous alcohol in brown needles, m. p. 184° (Found : Br, 53·1. $C_{12}H_7O_2N_2Br_3$ requires Br, 53·0%). It gave a mixture of mono- and di-bromo-*p*-aminophenols on reduction, and by further bromination, 3 : 5 : 3′ : 5′-tetrabromo-4 : 4′-dihydroxyazobenzene, the constitution of which has been proved.

3 : 5 : 3′-*Tribromo*-4 : 4′-*diacetoxyazobenzene* crystallised from

alcohol in light brown prisms, m. p. 172°, and the *dibenzoyl* derivative from benzene in yellow needles, m. p. 216°.

3 : 5 : 3′ : 5′-Tetrabromo-4 : 4′-dihydroxyazobenzene was obtained as yellow-brown needles, m. p. 252° (decomp.), from acetic acid (Found: Br, 60·4. Calc.: Br, 60·4%), and was identical with the substance described by Weselsky and Benedikt (*loc. cit.*); it yielded 2 : 6-dibromo-4-aminophenol, m. p. 190°, on reduction. The *diacetyl* derivative formed yellow granules, m. p. 240°, from benzene, and the *dibenzoyl* derivative orange needles, m. p. 265°.

3 : 3′-Dichloro-5 : 5′-dibromo-4 : 4′-dihydroxyazobenzene. 3 : 3′-Dichloro-4 : 4′-dihydroxyazobenzene was brominated completely, with 2 equivs. of the brominating agent, in 15 minutes, and a quantity of the product separated; the remainder was obtained by dilution with water. It crystallised from alcohol in fine yellowish-red needles, m. p. 262° (Found: Ag halides/original weight, 151·7. $C_{12}H_6O_2N_2Cl_2Br_2$ requires 150·4%). It reduced to 2-chloro-6-bromo-4-aminophenol, m. p. 177° (decomp.) (compare Raiford, *Amer. Chem. J.*, 1911, **46**, 422).

Action of Iodine Chloride on p-*Azophenol.*—Solutions of *p*-azophenol (1 g.) in stable acetic acid (230 c.c.) and of dichloramine-T (0·6 g.) and potassium iodide (0·72 g.) in acetic acid (50 c.c.) were mixed. After 25 minutes the iodine chloride had disappeared and purple granules were deposited (0·8 g.) which crystallised from alcohol in bluish-black needles, m. p. 185° (Found: N, 12·8. Calc.: N, 13·2%). The compound was identified as the quinhydroneazine (Willstätter and Benz, *Ber.*, 1906, **39**, 3482) by reduction with sulphur dioxide to *p*-azophenol (m. p. 204°), by stronger reduction to *p*-aminophenol (m. p. 183°), by oxidation in dry ether solution with dry silver oxide to quinoneazine (m. p. 158°), and by a mixed melting-point determination with an authentic specimen prepared by the method of these authors. The same substance was given by the action of excess of the iodinating agent on *p*-azophenol.

Derivatives of o-*Azophenol* (2 : 2′-*Dihydroxyazobenzene*).—*5-Chloro-2 : 2′-dihydroxyazobenzene* formed fine brown granules, m. p. 164°, from aqueous alcohol (Found: Cl, 14·4. $C_{12}H_9O_2N_2Cl$ requires Cl, 14·3%). Its constitution was decided by further chlorination to 5 : 5′-dichloro-2 : 2′-dihydroxyazobenzene.

5-Chloro-2 : 2′-diacetoxyazobenzene crystallised from alcohol in fine orange needles, m. p. 117°, and the *dibenzoyl* derivative in brown prisms, m. p. 119°.

5 : 5′-Dichloro-2 : 2′-dihydroxyazobenzene was obtained in orange-yellow needles, m. p. 267°, from alcohol (Found: Cl, 25·2. $C_{12}H_8O_2N_2Cl_2$ requires Cl, 25·1%). On reduction with stannous chloride and hydrochloric acid and removal of tin, a hydrochloride

was *obtained* which was immediately converted into the acetyl compound by means of acetic anhydride and sodium acetate. The product formed white needles, m. p. 170°, from alcohol, and was proved to be 4-*chloro-2-acetamidophenyl acetate* (Found : Cl, 14·5 $C_{10}H_{10}O_3NCl$ requires Cl, 15·6%) by comparison with the compound (m. p. and mixed m. p. 170°) produced by the reduction and subsequent acetylation of *p*-chloro-*o*-nitrophenol.

5 : 5′-*Dichloro-2 : 2′-diacetoxyazobenzene* crystallised in orange-red needles, m. p. 199°, from alcohol, and the *dibenzoyl* derivative formed pale brown needles, m. p. 243°.

3 : 5 : 5′-Trichloro-2 : 2′-dihydroxyazobenzene was obtained by the usual method as orange needles, m. p. 235°, from benzene, identical with the product prepared by the method of Bohn and Heumann (*loc. cit.*). Its constitution was proved by its further chlorination to the 3 : 5 : 3′ : 5′-tetrachloro-compound. The *diacetyl* derivative crystallised from alcohol in pale orange prisms m. p. 189°, and the *dibenzoyl* derivative in yellow-brown granules, m. p. 247°, from benzene.

3 : 5 : 3′ : 5′-*Tetrachloro-2 : 2′-dihydroxyazobenzene* formed silky, orange-red needles, m. p. 246—247°, from benzene (Found : Cl, 40·2. $C_{12}H_6O_2N_2Cl_4$ requires Cl, 40·4%). By reduction with stannous chloride a *hydrochloride* (Found : Cl as chloride, 16·2; total Cl, 50·1. $C_6H_5ONCl_2,HCl$ requires Cl as chloride, 16·5; total Cl, 49·6%) was obtained. The corresponding *base*, m. p. 107° (decomp.), was identical with 2 : 4-*dichloro-6-aminophenol*, m. p. 109° (decomp.), prepared by the reduction of 2 : 4-dichloro-6-nitrophenol (Fischer, *Annalen*, 1870, Spt. 7, 193). A mixture of the two specimens had m. p. 107°.

3 : 5 : 3′ : 5′-*Tetrachloro-2 : 2′-diacetoxyazobenzene* crystallised from alcohol in pink needles, m. p. 195°, and the *dibenzoyl* derivative in yellowish-brown prisms, m. p. 186°.

5-*Bromo-2 : 2′-dihydroxyazobenzene* formed a brown, microcrystalline solid, m. p. 154°, from aqueous alcohol (Found : Br, 27·1. $C_{12}H_9O_2N_2Br$ requires Br, 27·3%). Further bromination gave the 5 : 5′-dibromo-compound.

5-*Bromo-2 : 2′-diacetoxyazobenzene* formed dark orange needles, m. p. 142°, and 5-*bromo-2 : 2′-dibenzoyloxyazobenzene* crystallised from benzene in light brown needles, m. p. 215°.

5 : 5′-*Dibromo-2 : 2′-dihydroxyazobenzene* was obtained from alcohol in orange-red needles, m. p. 249° (Found : Br, 42·65. $C_{12}H_8O_2N_2Br_2$ requires Br, 43·0%). On reduction it gave *p*-bromo-*o*-aminophenol hydrochloride (Found : Ag halides/original weight, 146·8. Calc., 147·6%), from which the base was obtained as a white

crystalline solid, m. p. 87° (Schlieper, *Ber.*, 1893, **26**, 2469, records m. p. 88°).

5 : 5′-*Dibromo*-2 : 2′-*diacetoxyazobenzene* crystallised from benzene in orange granules, m. p. 211°, and the *dibenzoyl* derivative in pale brown needles, m. p. 202°.

3 : 3′ : 5 : 5′-Tetrabromo-2 : 2′-dihydroxyazobenzene obtained by the chloroamine method of bromination formed orange-brown needles, m. p. 262°, from benzene (Found: Br, 59·7. Calc.: Br, 60·3%), identical with the substance prepared by Weselsky and Benedikt's method (*loc. cit.*). Its constitution was assumed by these authors, but has now been established by reduction of the compound to 2 : 4-dibromo-6-aminophenol, m. p. 97—98° (Thiele and Eichwede, *Annalen*, 1900, **311**, 373, gave m. p. 98—99°), the hydrochloride of which was analysed for halogen (Found: Ag halides/original weight, 170·5. Calc., 171·2%).

3 : 5 : 3′ : 5′-*Tetrabromo*-2 : 2′-*diacetoxyazobenzene* crystallised from benzene in brown granules, m. p. 210—211°, and the *dibenzoyl* derivative in coarse orange granules, m. p. 214°.

5-*Iodo*-2 : 2′-*dihydroxyazobenzene*. *o*-Azophenol (2 g.) was dissolved in stable acetic acid (200 c.c.), and a solution of 33% excess over one equivalent of iodinating agent added. The latter was generated by adding finely powdered potassium iodide (2·1 g.) slowly with shaking to a solution of dichloramine-T (1·5 g.) in acetic acid (100 c.c.). The mixture was gently warmed on the water-bath, and the course of the reaction was followed by titrating 10 c.c. of the mixture at 10-minute intervals with thiosulphate. When the titre had fallen to one-quarter of the original value, the mixture was cooled and the excess of iodine was destroyed by addition of a solution of sodium sulphite. Dilution with water yielded a brown precipitate which crystallised from alcohol in brown needles (2·2 g.), m. p. 149—150° (Found: I, 37·3. $C_{12}H_9O_2N_2I$ requires I, 37·4%). Further iodination yielded the 5 : 5′-di-iodo-compound.

5-*Iodo*-2 : 2′-*diacetoxyazobenzene* crystallised from benzene in brown prisms, m. p. 138°, and the *dibenzoyl* derivative from alcohol in pale brown needles, m. p. 159°.

5 : 5′-*Di-iodo*-2 : 2′-*dihydroxyazobenzene*, prepared by the treatment of *o*-azophenol with two equivalents of iodinating agent, crystallised from alcohol in brown needles, m. p. 153° (Found: I, 54·2. $C_{12}H_8O_2N_2I_2$ requires I, 54·5%).

Reduction yielded the *hydrochloride* of *p*-*iodo*-*o*-*aminophenol* (Found: Ag halides/original weight, 138·8. C_6H_7ONClI requires 139·4%), from which the *base* was obtained in white needles, m. p.

139°; it was identical with the product formed by reducing *p*-iodo-*o*-nitrophenol.

5 : 5′-*Di-iodo*-2 : 2′-*diacetoxyazobenzene* formed dark brown granules, m. p. 145°, from alcohol, and the *dibenzoyl* derivative pale brown needles, m. p. 147°.

3 : 5 : 3′ : 5′-*Tetraiodo*-2 : 2′-*dihydroxyazobenzene* was obtained in the usual way in brown needles, m. p. 98—99°, from benzene (Found: I, 70·65. $C_{12}H_6O_2N_2I_4$ requires I, 70·8%). On reduction it gave the *hydrochloride* of 2 : 4-*di-iodo*-6-*aminophenol* (Found: Ag halides/original weight, 157·1. $C_6H_5ONI_2$,HCl requires 154·4%), from which the *base* was obtained as white needles, m. p. 120°, identical with the substance obtained by the reduction of 2 : 4-di-iodo-6-nitrophenol; a mixture of the two substances melted at 120·5°.

3 : 5 : 3′ : 5′-*Tetraiodo*-2 : 2′-*dibenzoyloxyazobenzene* formed grey-brown needles, m. p. 241°, from alcohol. The corresponding diacetyl compound was not prepared, since hot acetic anhydride caused decomposition of the azophenol.

Analytical Note.—In this and the following paper mixed-halogen analyses were conducted by the Carius method, and expressed either as percentages of each halogen or as a percentage ratio of the weight of the mixed silver halides to the original weight of the substance, according to whether or not the mixed silver halides were converted into silver chloride and reweighed.

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BANGOR. [*Received, May* 26*th*, 1928.]

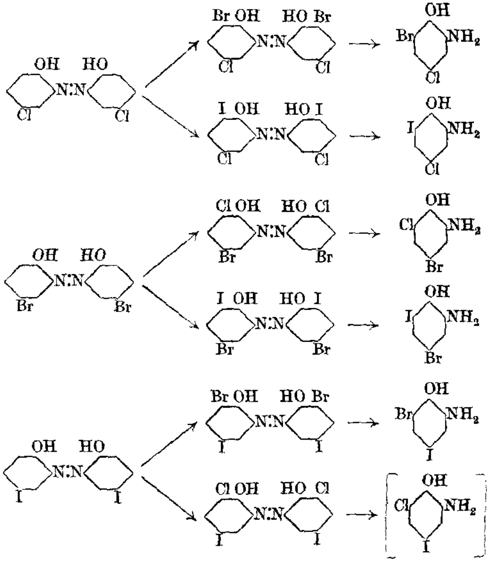
CCLXVIII.—*The Preparation of Some Halogenoaminophenols. Part I. Mixed Tetrahalogen Derivatives of* o-*Azophenol. Part II. Halogen Derivatives of* p-*Hydroxyazobenzene.*

By LOUIS HUNTER and RONALD SIDNEY BARNES.

Part I. Mixed Tetrahalogen Derivatives of o-*Azophenol.*

THE method employed for the preparation of substituted aminophenols in this research is based on the ease of reduction of *o*- and *p*-azophenol and their derivatives (see preceding paper). It has been shown (*loc. cit.*) that the primary product of the reaction between two molecules of halogen and one of *o*-azophenol is the 5 : 5′-disubstituted compound, and that further halogenation fills the 3- and 3′-positions. This property allows of the preparation of two isomerides of each of dichlorodibromo-, dichlorodi-iodo-,

and dibromodi-iodo-*o*-azophenol, the reduction of which should give rise to the six theoretically possible mixed 2 : 4-dihalogeno-6-aminophenols; five are described in this paper.



In the preparation of the mixed tetrahalogeno-*o*-azophenols it was not usually necessary to isolate the dihalogen compound from the solvent medium, since, by using the calculated quantity of halogonating agent, substitution of one halogen for hydrogen could be followed by substitution of a second in the same solution. In the case of the *5 : 5′*-di-iodo-compounds, however, preliminary isolation of the di-iodo-stage was essential, since it is usual to employ excess of the iodinating agent, the excess being ultimately removed by addition of sodium sulphite. Use of a further quantity of chloroamine in the same solution, whether for chlorination or bromination, would naturally lead to further iodination.

EXPERIMENTAL.

The same methods of halogenation were used as in the preceding work, although in some cases acetochloroamide was employed instead of dichloramine-T as a source of halogen. The advantage of the former is that its product of hydrolysis (acetamide) is soluble in water, and therefore does not contaminate the halogenated material when this is isolated from acetic acid solution by dilution with water. Analyses are expressed as before (*loc. cit.*, analytical note).

5 : 5'-*Dichloro*-3 : 3'-*dibromo*-2 : 2'-*dihydroxyazobenzene*. — o-Azophenol (2 g.) dissolved in stable acetic acid (500 c.c.) was chlorinated to the dichloro-stage by the addition of a solution of dichloramine-T (2·3 g.) in acetic acid (100 c.c.) with the addition of a few drops of dilute hydrochloric acid. When free chlorine could no longer be detected (20 minutes), the solution was reduced to about half its bulk by distillation under reduced pressure. Bromination was then effected by adding to the warmed mixture a solution of dichloramine-T (2·55 g.) in acetic acid (50 c.c.) to which had been added potassium bromide (2·25 g.) in water (10 c.c.). When the mixture was cooled, the *chlorobromo*-compound separated in orange-red prisms. A further quantity was obtained by removing part of the solvent by distillation under diminished pressure. It crystallised from benzene in needles of the same colour, m. p. 259° (decomp.); yield, 3·0 g. (Found: Cl, 15·3; Br, 36·7. $C_{12}H_6O_2N_2Cl_2Br_2$ requires Cl, 16·1; Br, 36·3%).

The *diacetyl* derivative crystallised from alcohol in pale orange needles, m. p. 203°, and the *dibenzoyl* derivative formed fine orange granules, m. p. 212°, from benzene and ligroin.

4-*Chloro*-6-*bromo*-2-*aminophenol*. — The above azophenol was decolorised with a warm mixture of stannous chloride and hydrochloric acid. After removal of tin from the solution with hydrogen sulphide, the residue yielded small white, prismatic crystals of the *aminophenol hydrochloride* (Found: Cl, 27·1; Br, 30·8. $C_6H_5ONClBr,HCl$ requires Cl, 27·4; Br, 30·9%). The *base*, liberated from the hydrochloride by means of aqueous sodium bicarbonate, formed fine white needles, m. p. 89—90°, from aqueous alcohol.

4-*Chloro*-6-*bromo*-2-*acetamidophenyl acetate* formed fine white needles, m. p. 130° (Found: Ag halides/original weight, 107·5. $C_{10}H_9O_3NClBr$ requires 108·1%), and 4-*chloro*-6-*bromo*-2-*benzamidophenyl benzoate* silky white needles, m. p. 180·5° (Found: Ag halides/original weight, 76·38. $C_{20}H_{13}O_3NClBr$ requires 76·98%), from aqueous alcohol.

3 : 3'-*Dichloro*-5 : 5'-*dibromo*-2 : 2'-*dihydroxyazobenzene*, prepared from *o*-azophenol, in a similar manner to its isomeride above, by bromination followed by chlorination, crystallised from benzene in fine orange-red needles, m. p. 263° (Found : Cl, 15·9 ; Br, 36·4%).

The *diacetyl* derivative crystallised from benzene in silky orange needles, m. p. 199°, and the *dibenzoyl* derivative from benzene and ligroin as an orange powder, m. p. 201°.

6-*Chloro*-4-*bromo*-2-*aminophenol* was obtained as its *hydrochloride* (Found : Cl, 27·4 ; Br, 31·6%) by reduction of the above azophenol with stannous chloride and hydrochloric acid. The *base* crystallised from aqueous alcohol in white prisms, m. p. 93°.

6-*Chloro*-4-*bromo*-2-*acetamidophenyl acetate* formed white prisms, m. p. 137°, from alcohol (Found : Ag halides/original weight, 108·3%), and 6-*chloro*-4-*bromo*-2-*benzamidophenyl benzoate* crystallised in silky white needles, m. p. 182° (Found : Ag halides/original weight, 76·05%).

5 : 5'-*Dichloro*-3 : 3'-*di-iodo*-2 : 2'-*dihydroxyazobenzene*.—*o*-Azophenol (2 g.) was chlorinated to the dichloro-stage, the solvent acetic acid (600 c.c.) was reduced by distillation to one-third of its bulk, and the dichloro-compound was then iodinated without isolation by the addition of a solution of iodine chloride (2·33 mols.) prepared by dissolving acetochloroamide (2·35 g.) and potassium iodide (4·2 g.) in acetic acid (150 c.c.). The whole solution was made up to 500 c.c. with acetic acid and warmed on a water-bath, specimens of 5 c.c. being withdrawn at 5-minute intervals. After 90 minutes the titre showed that two molecules of iodine chloride had been used, and the solution was cooled and the excess of iodine destroyed by the addition of aqueous sodium sulphite. On removal of the bulk of the solvent by distillation, the dichlorodi-iodo-compound separated as a brown precipitate. A further quantity was obtained by diluting the filtrate with water. It formed orange-yellow needles (4·1 g.) from benzene, which on heating rapidly had m. p. 272° (decomp.) (Found : Cl, 13·1 ; I, 47·4. $C_{12}H_6O_2N_2Cl_2I_2$ requires Cl, 13·3 ; I, 47·5%).

The *diacetyl* derivative crystallised from benzene in silky orange needles, m. p. 205°, and the *dibenzoyl* derivative in light brownish needles, m. p. 254°.

4-*Chloro*-6-*iodo*-2-*aminophenol* was obtained, by the reduction of the above azophenol, in the form of its *hydrochloride*, which crystallised from water in small white prisms (Found : Cl, 23·3 ; I, 40·6. C_6H_5ONClI,HCl requires Cl, 23·2 ; I, 41·5%). The *base* formed white needles from aqueous alcohol, having no definite melting point but charring at about 90°.

4-*Chloro*-6-*iodo*-2-*acetamidophenyl acetate* formed silky white

needles, m. p. 169°, from aqueous alcohol (Found: Ag halides original weight, 107·9. $C_{10}H_9O_3NClI$ requires 107·1%).

5 : 5'-Dibromo-3 : 3'-di-iodo-2 : 2'-dihydroxyazobenzene was prepared from *o*-azophenol by bromination followed by iodination as in the preceding example. It crystallised from alcohol in light brown needles (yield, 83%), m. p. 255° (decomp.) (Found: Ag halides/original weight, 134·8. $C_{12}H_6O_2N_2Br_2I_2$ requires 135·6%).

The *diacetyl* derivative crystallised from benzene and ligroin in pale orange needles, *m.* p. 186°, and the *dibenzoyl* derivative in pale brown needles, *m. p.* 252°.

4-Bromo-6-iodo-2-aminophenol hydrochloride, produced by the reduction of the above dibromodi-iodo-compound, formed creamy white flakes (Found: Cl, 10·1; Br, 22·95; I, 35·8. C_6H_5ONBrI,HCl requires Cl, 10·1; Br, 22·8; I, 36·2%). The *base* crystallised from alcohol in fine white needles which decomposed before melting.

4-Bromo-6-iodo-2-acetamidophenyl acetate crystallised from alcohol in silky white needles, m. p. 190° (decomp.) (Found: Ag halides/original weight, 106·7. $C_{10}H_9O_3NBrI$ requires 106·3%), and *4-bromo-6-iodo-2-benzamidophenyl benzoate* from aqueous alcohol in white prisms, m. p. 185° (Found: Ag halides/original weight, 80·9. $C_{20}H_{13}O_3NBrI$ requires 81·02%).

3 : 3'-Dibromo-5 : 5'-di-iodo-2 : 2'-dihydroxyazobenzene.—5 : 5'-Di-iodo-2 : 2'-dihydroxyazobenzene was isolated as described in the previous paper. It was then brominated with two equivalents of the brominating agent, and the dibromodi-iodo-compound was isolated as orange-red needles, m. p. 256°, after three crystallisations from benzene (Found: Br, 25·9; I, 40·2. $C_{12}H_6O_2N_2Br_2I_2$ requires Br, 25·6; I, 40·7%).

The *diacetyl* derivative crystallised from benzene in golden needles, m. p. 217°, and the *dibenzoyl* derivative in orange-red prisms, m. p. 215°.

6-Bromo-4-iodo-2-aminophenol was obtained by reduction of the above azophenol with stannous chloride and hydrochloric acid, removal of the tin, and decolorisation of the solution by boiling with animal charcoal, as its *hydrochloride* (Found: Ag halides/original weight, 162·9. C_6H_5ONBrI,HCl requires 161·5%), white, crystalline flakes. The *base* formed needles, m. p. 90°, from alcohol.

6-Bromo-4-iodo-2-acetamidophenyl acetate crystallised from aqueous alcohol in pearl-white, silky needles, m. p. 196° (Found: Ag halides/original weight, 106·7. $C_{10}H_9O_3NBrI$ requires 106·3%), and *6-bromo-4-iodo-2-benzamidophenyl benzoate* in fine white needles, m. p. 194—195° (Found: Ag halides/original weight, 80·67. $C_{20}H_{13}O_3NBrI$ requires 81·02%).

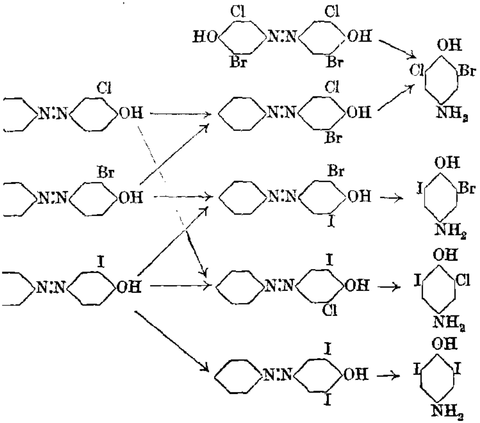
3 : 3'-Dichloro-5 : 5'-di-iodo-2 : 2'-dihydroxyazobenzene.—Repeated

ttempts to chlorinate 5 : 5'-di-iodo-2 : 2'-dihydroxyazobenzene as escribed above, with two equivalents of chlorinating agent, yielded dark brown, amorphous powder which could not be crystallised, nd decomposed above 200° without melting. Although its nalysis approximated to that calculated for $C_{12}H_6O_2N_2Cl_2I_2$, it was ot considered sufficiently pure to be used for the preparation of erivatives, or for reduction to the corresponding aminophenol.

Part II. Halogen Derivatives of p-*Hydroxyazobenzene.*

As iodo-*p*-azophenols could not be prepared (preceding paper), dine-substituted *p*-aminophenols were obtained by reducing the do-derivatives of *p*-hydroxyazobenzene, which are readily accesble; they were separated from the aniline simultaneously formed y means of the difference in solubility of the hydrochlorides.

Direct halogenation of *p*-hydroxyazobenzene gave the 3 : 5-dilogeno-compounds (compare Hewitt and Aston, J., 1900, 77, 12, 810). The monohalogen derivatives were therefore synthesised y coupling diazotised aniline with the *o*-halogenophenols.



The duplicate methods of preparation of the mixed dihalogenompounds (see scheme) place beyond doubt their constitution and at of the aminophenols derived from them.

EXPERIMENTAL.

The dihalogen derivatives of *p*-hydroxyazobenzene described below were prepared by the chloroamine method.

3-*Chloro*-4-*hydroxyazobenzene* was obtained (yield, 70%) by coupling benzenediazonium chloride with *o*-chlorophenol. It crystallised from aqueous alcohol in yellow prisms, m. p. 88·5° (Farmer and Hantzsch, *Ber.*, 1899, **32**, 3089, give m. p. 88°).

3-*Bromo*-4-*hydroxyazobenzene*.—Carefully purified *o*-bromophenol was coupled with the required quantity of diazotised aniline, the mixture being kept strongly alkaline to prevent precipitation of the hydrochloride of the azo-compound. When coupling was complete, the solution was cautiously neutralised by the addition during some hours of dilute acetic acid; rapid neutralisation precipitated the azo-compound as an oil. The solid product crystallised from light petroleum in fine yellow needles, m. p. 80°; yield, 90% (Found: Br, 28·7. $C_{12}H_9ON_2Br$ requires Br, 28·9%). It gave a purple-brown crystalline *hydrochloride*, m. p. 159°. The *acetyl* derivative formed yellow-brown plates, m. p. 98° (Found: Br, 24·9. $C_{14}H_{11}O_2N_2Br$ requires Br, 25·1%), and the *benzoyl* derivative crystallised from aqueous alcohol in brown needles, m. p. 113° (Found: Br, 21·0. $C_{19}H_{13}O_2N_2Br$ requires Br, 21·0%).

3-*Iodo*-4-*hydroxyazobenzene*, prepared (yield, 85%) by a method analogous to that described for the bromo-compound, crystallised from light petroleum as yellow flakes, m. p. 77—78°, darkening somewhat on exposure (Found: I, 39·1. $C_{12}H_9ON_2I$ requires I, 39·2%). It formed a blue-black *hydrochloride*, m. p. 172° (decomp.); an *acetyl* compound, crystallising in slender orange needles, m. p. 103—104° (Found: I, 34·9. $C_{14}H_{11}O_2N_2I$ requires I, 34·7%); and a *benzoyl* derivative, crystallising from alcohol in pale orange needles, m. p. 105° (Found: I, 30·1 $C_{19}H_{13}O_2N_2I$ requires I, 29·7%).

3-*Chloro*-5-*bromo*-4-*hydroxyazobenzene*.—(*a*) 3-Chloro-4-hydroxyazobenzene (1·5 g.) was dissolved in stable acetic acid (40 c.c.) and treated with a solution of acetochloroamide (0·6 g.) in acetic acid (30 c.c.) to which had been added potassium bromide (1·5 g.) in water (10 c.c.). The *chlorobromo*-compound soon began to separate in fine orange needles, which crystallised from aqueous acetic acid in the same form, m. p. 125·5°. A further crop was obtained by diluting the mixture with water; total yield, 1·6 g. (Found: Ag halides/original weight, 105·9. $C_{12}H_8ON_2ClBr$ requires 106·4%).

(*b*) A solution of 5-bromo-4-hydroxyazobenzene (4·0 g.) in acetic acid (35 c.c.) was chlorinated by the addition of a solution of dichloramine-T (1·8 g.) in acetic acid (15 c.c.) and a few drops of dilute hydrochloric acid. Separation of the product commenc

immediately, and chlorination was complete in ½ hour. A further crop was obtained by diluting the solution with an equal volume of water; total yield, 3·5 g., m. p. 125°. A mixture with the substance prepared by method (*a*) had m. p. 125·0°.

The *acetyl* derivative crystallised from aqueous alcohol in orange-brown needles, m. p. 133·5° (Found: Ag halides/original weight, 93·43. $C_{14}H_{10}O_2N_2ClBr$ requires 93·76%), and the *benzoyl* derivative from benzene and ligroin in orange prisms, m. p. 118·5° (Found: Ag halides/original weight, 79·12. $C_{19}H_{12}O_2N_2ClBr$ requires 79·75%).

As a final proof of the constitution of the chlorobromo-*p*-hydroxyazobenzene, specimens reduced with stannous chloride and hydrochloric acid yielded 2-chloro-6-bromo-4-aminophenol, m. p. 177° (decomp.), identical with the substance prepared as described on p. 2055.

2-*Chloro-6-bromo-4-acetamidophenyl acetate* crystallised from alcohol in fine white needles, m. p. 168·5° (Found: Ag halides/original weight, 107·1. $C_{10}H_9O_3NClBr$ requires 107·9%), and 2-*chloro-6-bromo-4-benzamidophenyl benzoate* in white platelets, m. p. 111—112° (Found: Ag halides/original weight, 76·65. $C_{20}H_{13}O_3NClBr$ requires 76·81%).

3-*Chloro-5-iodo-4-hydroxyazobenzene*.—(*a*) The chlorination of 5-iodo-4-hydroxyazobenzene was conducted in the usual way in acetic acid solution, dichloramine-T (1 equiv.) being used in the presence of a few drops of dilute hydrochloric acid. The product (yield, 60%) crystallised from ligroin as a fine brown powder, m. p. 110·5° (Found: Cl, 9·5; I, 35·5. $C_{12}H_8ON_2ClI$ requires Cl, 9·9; I, 35·4%).

(*b*) 3-Chloro-4-hydroxyazobenzene (5 g.) dissolved in acetic acid (150 c.c.) was treated with a solution of iodine chloride (1 mol.) generated by shaking together acetochloroamide (2·75 g.), finely powdered potassium iodide (4 g.), and acetic acid (100 c.c.). The mixture was warmed on the water-bath until the titre had fallen to one-quarter of the original value. The excess of iodine was removed by sodium sulphite, the bulk of the solvent distilled off under diminished pressure, and the residue diluted with water (100 c.c.). The product precipitated crystallised from ligroin in fine brown granules, m. p. 110°; yield, 5·3 g.

A mixture of the two specimens melted at 110°. 3-*Chloro-5-iodo-4-acetoxyazobenzene* crystallised from alcohol in fine orange-red needles, m. p. 124° (Found: Ag halides/original weight, 94·77. $C_{14}H_{10}O_2N_2ClI$ requires 94·5%), and 3-*chloro-5-iodo-4-benzoyloxyazobenzene* from benzene in orange prisms, m. p. 115° (Found: Ag halides/original weight, 82·04. $C_{19}H_{12}O_2N_2ClI$ requires 81·9%).

2-*Chloro-6-iodo-4-aminophenol* was obtained together with aniline

by the reduction of the above chloroiodo-*p*-hydroxyazobenzene with stannous chloride. On removal of the tin from the resulting mixture, the less soluble *2-chloro-6-iodo-4-aminophenol hydrochloride* (Found: Ag halides/original weight, 170·2. C_6H_5ONClI,HCl requires 170·6%) separated in white needles, from which the base was obtained by treatment with sodium bicarbonate in silky white prisms, m. p. 169° (decomp.).

2-Chloro-6-iodo-4-acetamidophenyl acetate, m. p. 155° (Found: Ag halides/original weight, 106·7. $C_{10}H_9O_3NClI$ requires 107·1%), and *2-chloro-6-iodo-4-benzamidophenyl benzoate*, m. p. 157° (Found: Ag halides/original weight, 80·28. $C_{20}H_{13}O_3NClI$ requires 79·93%), crystallised from aqueous alcohol in needles.

3-Bromo-5-iodo-4-hydroxyazobenzene.—(*a*) 5-Iodo-4-hydroxyazobenzene was treated with one equivalent of the brominating agent prepared by mixing the required quantities of aqueous potassium bromide and an acetic acid solution of dichloramine-T. The halogen soon disappeared, and dilution with water then precipitated the *bromoiodo*-compound, which crystallised from ligroin in orange-brown needles, m. p. 128·5° (Found: Br, 19·8; I, 31·4. $C_{12}H_8ON_2BrI$ requires Br, 19·9; I, 31·5%).

(*b*) A solution of 3-bromo-4-hydroxyazobenzene was treated in acetic acid solution on the water-bath with iodine chloride (1 mol.) prepared as before, until the titre showed that one equivalent of iodinating agent had been used. Dilution of the solution with water, and crystallisation of the amorphous precipitate from alcohol, followed by ligroin, afforded an orange-brown, crystalline material, m. p. 128·5°. Mixed with the specimen obtained above, it melted at 128°.

3-Bromo-5-iodo-4-acetoxyazobenzene crystallised from alcohol in silky, orange needles, m. p. 127—128° (Found: Ag halides/original weight, 95·32. $C_{14}H_{10}O_2N_2BrI$ requires 95·08%), and *3-bromo-5-iodo-4-benzoyloxyazobenzene* in brown prisms, m. p. 85° (Found: Ag halides/original weight, 82·56. $C_{19}H_{12}O_2N_2BrI$ requires 83·43%)

2-Bromo-6-iodo-4-aminophenol.—Loss of iodine resulted on boiling the above bromoiodo-*p*-hydroxyazobenzene with acid stannous chloride, but smooth reduction was achieved by treatment of the azo-compound with an acetic acid solution of stannous chloride prepared by passing dry hydrogen chloride into a mixture of tin and acetic acid until the tin had dissolved. The aminophenol was isolated in the usual way as its *hydrochloride* (Found: Cl, 10·05 Br, 22·8; I, 36·0. C_6H_5ONBrI,HCl requires Cl, 10·1; Br, 22·8 I, 36·2%), from which the base was obtained by the action of sodium bicarbonate in short white prisms, m. p. 185° (decomp.).

2-Bromo-6-iodo-4-acetamidophenyl acetate crystallised from aqueous

alcohol in slender needles, m. p. 186° (Found: Ag halides/original weight, 105·9. $C_{10}H_9O_3NBrI$ requires 106·3%), and 2-*bromo-6-iodo-4-benzamidophenyl benzoate* in plates, m. p. 148° (Found: Ag halides/original weight, 80·52. $C_{20}H_{13}O_3NBrI$ requires 81·02%).

3 : 5-*Di-iodo-4-hydroxyazobenzene.*—Attempts to prepare this compound by direct iodination of *p*-hydroxyazobenzene were not successful, oxidation as well as iodination resulting.

To a solution of 3-iodo-4-hydroxyazobenzene (see p. 2064) (4 g.) in acetic acid (65 c.c.) was added a solution of iodine chloride (1 mol.) prepared by mixing together dichloramine-T (2 g.) in acetic acid (35 c.c.) and powdered potassium iodide (2·8 g.). The mixture was heated on the water-bath until the titre showed that one equivalent of iodinating agent had been used (6 minutes). The excess of iodine was then removed by aqueous sodium sulphite, and the product precipitated by the addition of water (100 c.c.). It crystallised from alcohol in brown needles, m. p. 128—129°; yield, 3·1 g. (Found: I, 56·9. $C_{12}H_8ON_2I_2$ requires I, 56·5%).

3 : 5-*Di-iodo-4-acetoxyazobenzene* crystallised from aqueous alcohol in orange-brown prisms, m. p. 162° (Found: I, 51·6. $C_{14}H_{10}O_2N_2I_2$ requires I, 51·6%), and 3 : 5-*di-iodo-4-benzoyloxyazobenzene* from acetic acid in fine, yellow needles, m. p. 137—139° (Found: I, 46·1. $C_{19}H_{12}O_2N_2I_2$ requires I, 45·8%).

Reduction of 3 : 5-*di-iodo-4-hydroxyazobenzene.* Cautious treatment of the azo-compound with an acetic acid solution of stannous chloride and hydrochloric acid afforded 2 : 6-di-iodo-4-aminophenol hydrochloride, from which the base was obtained by the addition of a saturated solution of sodium bicarbonate. It formed long white needles, m. p. 173°, from alcohol (Found: I, 70·3. Calc.: I, 70·4%). Raiford, Taft, and Lankelma (*J. Amer. Chem. Soc.*, 1924, **46**, 2051) give m. p. 169—171°.

3 : 5-*Di-iodo-4-acetamidophenyl acetate* forms silky, white needles, m. p. 209°, from alcohol (Found: I, 57·0. $C_{10}H_9O_3NI_2$ requires I, 57·1%).

Grateful acknowledgment is made to Dr. S. Sugden for a gift of o-iodonitrobenzene, to the Department of Scientific and Industrial Research for a grant which enabled one of the authors (R. S. B.) to take part in the work, and especially to Professor K. J. P. Orton, F.R.S., for the facilities he has provided and for the interest he has shown throughout the course of the work set forth in this and the preceding paper.

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CCLXIX.—*The Reaction between Acetylene and Sulphur at Temperatures up to 650°.*

By JOHN BUTTERY PEEL and PERCY LUCOCK ROBINSON.

MEYER and SANDMEYER (*Ber.*, 1883, **16**, 2176) obtained material, regarded as thiophen and giving the indophenin reaction, by heating sulphur in acetylene, but it is not stated that the substance was isolated. Capelle (*Bull. Soc. chim.*, 1908, **4**, 150) and de Coninck (*Bull. Acad. roy. Belg.*, 1908, 305) state that only carbon disulphide, thiophten, and a material with a garlic-like odour is present. Recent work (Briscoe and Peel, this vol., p. 1741) has indicated that thiophen is probably produced, and this work sought to determine roughly the composition of the liquid condensed at laboratory temperatures. The main reaction appears to yield carbon disulphide and hydrogen sulphide, but 77% of the sulphur at most is in the condensate, the rest probably converting the acetylene into carbon and hydrogen sulphide. Small quantities of thiophen and thiophten are formed at all the temperatures employed, 500° being the optimum, but benzene and naphthalene are entirely absent.

EXPERIMENTAL.

Preliminary.—Sulphur was heated in an ordinary distillation-flask, clamped horizontally, at the centre of which acetylene was delivered, and the products were passed through the side-limb into a bottle cooled in water and fitted with a reflux condenser. The phenomena observed were similar to those noted by Capelle (*loc. cit.*): the reaction, initiated by a dense yellow flame which deposited carbon, appeared to take place between the vapour and the gas at a temperature below the boiling point of sulphur; later, when there was a sufficiently constant supply of vapour, the acetylene burned steadily. The brown oily liquid from several runs was distilled through a spiral column until no further distillate could be obtained at 150°. The boiling point of the distillate gradually rose to a maximum of about 65°. The residue was distilled under reduced pressure and gave an orange liquid, b. p. 110—115°/20 mm., which on redistillation at the ordinary pressure gave a liquid, b. p. 210—220°, with the reactions of thiophten. The lighter fraction, when fractionated through a bead-filled column 4 feet long, yielded a large head fraction of carbon disulphide, b. p. 46·7°, and a fraction, amounting to 5%, b. p. 84·0°/760·5 mm. This proved to be thiophen, giving the indophenin and other reactions characteristic of that substance (Found: C, 57·1; H, 4·5. Calc.: C, 57·1; H, 4·8%). The carbon disulphide contained a trace of material with a

garlic-like odour which even the careful fractionation employed failed to isolate.

Addition of 5% of iron or 1% of iodine to the sulphur had little effect on the course of the reaction, the proportion of thiophen in the lighter fractions being 6% and 5% respectively.

In order to ascertain the lowest temperature at which the reaction began, the flask was surrounded by a double-walled air-bath, closed at the top with asbestos board, carrying a thermometer, and suitably cut for the neck of the flask. Ignition invariably took place at 275°, but after the first flash, if the temperature continued to be raised, no further flame formation took place even up to 325°. If, however, the flask were cooled below 275° and again raised above that point, flashing was once more observed. Below 300° the rate of reaction was inconveniently slow.

Reaction at about 325°.—Acetylene was led below the surface of the molten sulphur, the object being to obtain material at the lowest temperature (325° ± 5°) at which there was a reasonable rate of reaction. About 38% of the sulphur was converted into a brown oil which yielded CS_2 77%, C_4H_4S 9%, $C_6H_4S_2$ 6%.

Reaction at about 500°.—A convenient apparatus consisted of a Pyrex tube 22″ × 1·5″ heated to the required temperature in a cylindrical electric furnace 12″ long. The closed end of the tube which protruded 5″ from the furnace was charged with 50 g. of sulphur and a rapid stream of acetylene was delivered about the centre of the heated zone. About 74% of the sulphur was converted into a brown oil containing CS_2 77%, C_4H_4S 12%, $C_6H_4S_2$ 6%.

Reaction at about 650°.—It was clear that a definite change had taken place in the course of the reaction at this temperature, resulting in the production of more carbon which caused constant trouble by choking the end of the tube delivering acetylene. About 77% of sulphur was converted into a liquid containing CS_2 83%, C_4H_4S 5%, $C_6H_4S_2$ 3%.

Previous determinations of the density (Schiff, *Ber.*, 1885, **18**, 1601) and surface tension of thiophen are somewhat old, and these properties have been redetermined on the material (analysed above) after three further fractionations, glass pyknometers of about 10 c.c. capacity and a pair of carefully calibrated capillary tubes being used; $d_{4^\circ}^{20^\circ} = 1·0615$ and $\gamma = 32·58$ at 20°. These data give a molecular parachor of 189·0, from which may be deduced the parachor of sulphur, 46·5 (value for double bond = 23·2, C = 4·8, H = 17·1, five-membered ring = 8·5). This is in close agreement with the mean value, 46·3, derived from the data for carbon disulphide (Ramsay and Shields, J., 1893, **63**, 1089; Morgan and Thomssen, *J. Amer. Chem. Soc.*, 1911, **33**, 657; Harkins, Clark, and

Roberts, *ibid.*, 1920, **42**, 700) but differs appreciably from the value 50·7 obtained with ethyl mercaptan (Morgan and Chazal, *ibid.*, 1913, **35**, 1821).

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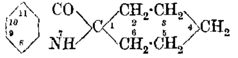
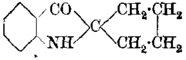
CCLXX.—*Derivatives of ψ-Indoxyl*spirocyclo*hexane.*

By RAYMOND LIVINGSTON BETTS and SYDNEY GLENN PRESTON PLANT.

IT has recently been shown that ψ-indoxyl*spirocyclo*hexane (I) and ψ-indoxyl*spirocyclo*pentane (II), although having many reactions in common, differ in some respects (Betts, Muspratt, and Plant, J., 1927, 1310), and it became clear that a study of some of the derivatives of the former would be interesting. By methods similar to those used in the synthesis of (I) we have now prepared 10-*methyl-*,

(I.) 

 (II.)

8-*methyl-*, 4-*methyl-*, and 8 : 10-*dimethyl-ψ-indoxyl*spirocyclo*hexane*, and have examined their reactions. The compounds (I) and (II) are each nitrated, even by dilute nitric acid, with remarkable ease to give a nitro-derivative, which, in the case of (I), is believed to be 10-nitro-ψ-indoxyl*spirocyclo*hexane. The methyl derivatives here described can all be nitrated with dilute nitric acid: the nitro-compounds form characteristic sodium derivatives in aqueous sodium hydroxide which are only sparingly soluble in cold water. The positions occupied by these nitro-groups are uncertain, but it seems probable that the 10-position is taken if possible, and the 8- if the former is not vacant. Attempts were made to reduce the nitro-group in some of these compounds with a view ultimately of introducing another substituent to give a substance which might be synthesised by methods similar to those used for making ψ-indoxyl*spirocyclo*hexane, but the isolation of the corresponding amino-compounds has not been brought about. There can, however, be little doubt that these nitro-groups are in the benzenoid part of the molecule, and this view is supported by the fact that the reactions

of these compounds, especially with aqueous sodium hydroxide, are similar to those of 1-nitro- and 3-nitro-tetrahydroacridone (Perkin and Sedgwick, J., 1924, **125**, 2438).

Although 10-methyl- and 4-methyl-ψ-indoxyl*spirocyclo*hexane can be readily converted by acetic anhydride into the corresponding 7-*acetyl* compounds, acetylation of the 8-methyl and 8 : 10-dimethyl derivatives by this reagent is much more difficult and requires the presence of a little concentrated sulphuric acid. This reluctance can be ascribed to the steric effect of the methyl group in the 8-position.

The alkylated 1-anilino*cyclo*hexane-1-carboxylic acids, from which the ψ-indoxyl*spirocyclo*hexane derivatives described in this paper were obtained by fusion with potassium hydroxide, all dissociate, on distillation, to yield the corresponding alkylated aniline and Δ^1-*cyclo*hexene-1-carboxylic acid, or, in the case of 1-*anilino-4-methyl*cyclo*hexane-1-carboxylic acid*, aniline and Δ^1-tetrahydro-*p*-toluic acid. This behaviour is similar to that of 1-anilino*cyclo*hexane-1-carboxylic acid itself, but differs completely from that of the analogous 1-anilino*cyclo*pentane-1-carboxylic acid (Plant and Facer, J., 1925, **127**, 2037).

EXPERIMENTAL.

10-*Methyl-ψ-indoxyl*spirocyclo*hexane*.—When a cooled solution of *p*-toluidine (24 g.) and *cyclo*hexanone (20 g.) in glacial acetic acid (100 c.c.) was treated with a concentrated aqueous solution of potassium cyanide (16 g.), 1-p-*toluidino*-1-*cyano*cyclo*hexane* separated in good yield; it was obtained from dilute alcohol in colourless needles, m. p. 76°. A solution of this nitrile (5 g.) in concentrated sulphuric acid (40 c.c.) was kept for 2 days at room temperature, then poured on ice and made alkaline with ammonia; 1-p-*toluidino*cyclo*hexane*-1-*carboxyamide* separated quantitatively. It crystallised from alcohol in colourless prisms, m. p. 156°. A mixture of the amide (5 g.) and concentrated hydrochloric acid (100 c.c.) was boiled under reflux for 8 hours and then evaporated to dryness. The residue was treated with hot aqueous sodium hydroxide (8%), the solution was filtered, and then acidified with glacial acetic acid. 1-p-*Toluidino*cyclo*hexane*-1-*carboxylic acid* separated in good yield and was obtained from dilute alcohol in colourless needles, m. p. 172° (Found: N, 5·8. $C_{14}H_{19}O_2N$ *requires* N, 6·0%). When the liquid obtained by distilling this acid from a distillation flask was treated with an excess of dilute hydrochloric acid, Δ^1-*cyclo*hexene-1-carboxylic acid, m. p. 29—31°, remained undissolved; the acid solution, on the addition of ammonia, yielded *p*-toluidine.

A mixture of 1-*p*-toluidino*cyclo*hexane-1-carboxylic acid (25 g.)

and potassium hydroxide (65 g.) was heated at 350—360° for ½ hour, allowed to cool, and then treated with an excess of water. The insoluble residue was dried over sulphuric acid in a desiccator and distilled, and the distillate crystallised from petroleum; *10-methyl-ψ-indoxyl*spiro*cyclohexane* was obtained in colourless prisms, m. p. 164° (Found: N, 6·4. $C_{14}H_{17}ON$ requires N, 6·5%). On boiling its solution in an excess of acetic anhydride for an hour and shaking the cooled product with water, *7-acetyl-10-methyl-ψ-indoxyl*spiro*cyclohexane* was obtained: it crystallised from methyl alcohol in colourless prisms, m. p. 144° (Found: C, 74·6; H, 7·5. $C_{16}H_{19}O_2N$ requires C, 74·7; H, 7·4%). This acetyl derivative is readily hydrolysed to the parent substance by boiling its solution in aqueous-alcoholic potassium hydroxide.

When a mixture of 10-methyl-ψ-indoxyl*spirocyclo*hexane (2 g.), water (40 c.c.), and nitric acid (10 c.c. of *d* 1·4) was boiled for 4 minutes, the solid gradually melted and a red oil appeared. The solution became yellow and, on cooling, the product appeared as a yellow solid. It was crystallised from alcohol, from which (?)*8-nitro-10-methyl-ψ-indoxyl*spiro*cyclohexane* separated in yellow prisms, m. p. 158° (Found: N, 10·8. $C_{14}H_{16}O_3N_2$ requires N, 10·8%).

*8-Methyl-ψ-indoxyl*spiro*cyclohexane*.—The preparation of this substance followed the course outlined above for the 10-methyl derivative. 1-o-*Toluidino*-1-*cyano*cyclo*hexane* separated from alcohol in colourless prisms, m. p. 72°, and 1-o-*toluidino*cyclo*hexane*-1-*carboxyamide* from dilute alcohol in colourless prisms, m. p. 143°. It was found advantageous to boil the solution of crude 1-o-*toluidino*cyclo*hexane*-1-*carboxylic acid* in very dilute aqueous sodium hydroxide for ½ hour with charcoal and then to acidify the filtered solution gradually by adding dilute acetic acid with constant stirring. The acid separated from dilute alcohol in colourless prisms, m. p. 117° (Found: N, 6·0. $C_{14}H_{19}O_2N$ requires N, 6·0%), and, on distillation, it dissociated into *o*-toluidine, identified as aceto-*o*-toluidide, and Δ^1-*cyclo*hexene-1-carboxylic acid. *8-Methyl-ψ-indoxyl*spiro*cyclohexane* was obtained from petroleum in colourless prisms, m. p. 197°. On boiling its solution in acetic anhydride, containing a few drops of concentrated sulphuric acid, for several hours and shaking the product with water, *7-acetyl-8-methyl-ψ-indoxyl*spiro*cyclohexane* was obtained as an oily mass, which solidified on being rubbed with ether; after being distilled under reduced pressure, the solid crystallised from methyl alcohol in colourless prisms, m. p. 226° (Found: N, 5·5. $C_{16}H_{19}O_2N$ requires N, 5·4%). (?)*10-Nitro-8-methyl-ψ-indoxyl*spiro*cyclohexane* can be obtained by boiling 8-methyl-ψ-indoxyl*spirocyclo*hexane with dilute nitric acid, but a more convenient method is to dissolve the substance in cold, con-

centrated nitric acid and, after 5 minutes, dilute the solution with water. It separates from alcohol in pale yellow prisms, m. p. 273—274° (Found: N, 10·7. $C_{14}H_{16}O_3N_2$ requires N, 10·8%).

8 : 10-*Dimethyl-ψ-indoxyl*spirocyclo*hexane*.—By methods similar to those described for the 8-methyl derivative the following products were isolated: 1-2′ : 4′-*Dimethylanilino*-1-*cyano*cyclo*hexane* from alcohol in colourless prisms, m. p. 115—116°, 1-2′ : 4′-*dimethylanilino*cyclo*hexane*-1-*carboxyamide* from dilute alcohol in colourless prisms, m. p. 133°, 1-2′ : 4′-*dimethylanilino*cyclo*hexane*-1-*carboxylic acid* (which dissociated into 2 : 4-dimethylaniline and Δ^1-*cyclo*hexene-1-carboxylic acid on distillation) from dilute alcohol in colourless prisms, m. p. 125° (Found: N, 5·7. $C_{15}H_{21}O_2N$ requires N, 5·7%), 8 : 10-*dimethyl-ψ-indoxyl*spirocyclo*hexane* from petroleum *in colourless prisms, m. p. 190°, and* 7-*acetyl*-8 : 10-*dimethyl-ψ-indoxyl*spirocyclo*hexane* from methyl alcohol in colourless plates, m. p. 96° (Found: N, 5·2. $C_{17}H_{21}O_2N$ requires N, 5·2%). When a mixture of 8 : 10-dimethyl-ψ-indoxyl*spirocyclo*hexane and dilute nitric acid was boiled for ½ hour, a *mononitro*-derivative was produced and this separated from alcohol in pale yellow prisms, m. p. 183—184° (decomp.) (Found: N, 9·9. $C_{15}H_{18}O_3N_2$ requires N, 10·2%).

4-*Methyl-ψ-indoxyl*spirocyclo*hexane*.—From 4-methyl*cyclo*hexanone and aniline by methods similar to those described under 10-methyl-ψ-indoxyl*spirocyclo*hexane the following substances were obtained: 1-*Anilino*-1-*cyano*-4-*methyl*cyclo*hexane* from dilute alcohol in colourless needles, m. p. 107°, 1-*anilino*-4-*methyl*cyclo*hexane*-1-*carboxyamide* from alcohol in colourless prisms, m. p. 161°, 1-*anilino*-4-*methyl*cyclo*hexane*-1-*carboxylic acid* from dilute alcohol in colourless prisms, m. p. 179° (Found: N, 6·2. $C_{14}H_{19}O_2N$ requires N, 6·0%), 4-*methyl-ψ-indoxyl*spirocyclo*hexane* from petroleum in colourless plates, m. p. 189° (Found: N, 6·5. $C_{14}H_{17}ON$ requires N, 6·5%), 7-*acetyl*-4-*methyl-ψ-indoxyl*spirocyclo*hexane* from methyl alcohol in colourless prisms, m. p. 102°, (?)10-*nitro*-4-*methyl-ψ-indoxyl*spirocyclo*hexane* from dilute alcohol in pale yellow prisms, m. p. 198° (Found: N, 10·9. $C_{14}H_{16}O_3N_2$ requires N, 10·8%), and (?)10-*nitro*-4 : 7-*dimethyl-ψ-indoxyl*spirocyclo*hexane* from dilute alcohol in pale yellow prisms, m. p. 141° (Found: N, 10·3. $C_{15}H_{18}O_3N_2$ requires N, 10·2%). The mixture obtained by distilling 1-anilino-4-methyl*cyclo*hexane-1-carboxylic acid, on treatment with dilute hydrochloric acid, yielded a solid which was readily soluble in aqueous sodium carbonate. This is clearly identical with the Δ^1-tetrahydro-*p*-toluic acid of Einhorn and Willstätter (*Annalen*, 1894, **280**, 163) and of Perkin and Pickles (J., 1905, **87**, 645), since it was obtained from dilute acetic acid in colourless needles, m. p.

134° (Found : C, 68·1 ; H, 8·4. Calc. : C, 68·6 ; H, 8·6%). The hydrochloric acid solution yielded aniline, identified as acetanilide, on being made alkaline with ammonia.

1-p-*Aminoanilino*cyclo*hexane*-1-*carboxylic Acid*.—A mixture of *p*-nitroaniline (14 g.), *cyclo*hexanone (12 g.), glacial acetic acid (200 c.c.), and potassium cyanide (10 g. in concentrated aqueous solution) was kept at 40—45° for 2 days, and then poured into dilute hydrochloric acid. 1-p-*Nitroanilino*-1-*cyano*cyclo*hexane*, which separated, was obtained from alcohol in pale yellow prisms, m. p. 134° (Found : N, 17·2. $C_{13}H_{15}O_2N_3$ requires N, 17·1%), and was hydrolysed in the usual way to 1-p-*nitroanilino*cyclo*hexane*-1-*carboxyamide*, isolated from alcohol in yellow prisms, m. p. 217° (Found : N, 16·0. $C_{13}H_{17}O_3N_3$ requires N, 16·0%), and then to 1-p-*nitroanilino*cyclo*hexane*-1-*carboxylic acid*, which separated from dilute alcohol in yellow plates, m. p. 201° (Found : N, 10·3. $C_{13}H_{16}O_4N_2$ requires N, 10·6%). The acid (3 g.), dissolved in dilute aqueous ammonia, was added to a mixture of ferrous sulphate (28 g. in concentrated aqueous solution) and ammonia (25 c.c. of *d* 0·880) at 90—95°, and, after being shaken at that temperature for ½ hour, the solution was filtered and just neutralised with glacial acetic acid. The 1-p-*aminoanilino*cyclo*hexane*-1-*carboxylic acid* which separated was obtained from aqueous pyridine in colourless needles, m. p. 216—217° (Found : N, 12·0. $C_{13}H_{18}O_2N_2$ requires N, 12·0%). The amino-acid decomposed completely on heating with potassium hydroxide alone or admixed with sodium ethoxide.

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CCLXXI.—*The Hydrolysis of Guanidine Carbonate.*

By JAMES BELL.

THE hydrolysis of guanidine in aqueous solution (Bell, J., 1926, 1213) at room temperature gives urea : $CN_3H_5 + H_2O = CON_2H_4 + NH_3$. This is also formed on boiling, but some of it is decomposed by the strongly alkaline solution owing to the dissociation of urea to ammonia and cyanic acid at the high temperature (Werner, J., 1918, **113**, 84). The cyanic acid is then fixed as guanidine cyanate, which is in turn hydrolysed to guanidine carbonate. The prepar-

ation of guanidine cyanate and a detailed examination of its hydrolysis will be dealt with in a future communication.

It is now shown that guanidine carbonate, when heated in aqueous solution to 100°, undergoes similar changes due to its dissociation into the free base and carbonic acid and hydrolysis of the former. A $N/10$-aqueous solution was unchanged after remaining for 10 weeks at room temperature. When it was boiled under reflux, hydrolysis took place to an appreciable extent; urea was first formed (1) and then decomposition to ammonium carbonate took place to a lesser degree (2).

$$(CN_3H_5)_2,H_2CO_3 + 2H_2O = 2CON_2H_4 + (NH_4)_2CO_3 \quad . \quad (1)$$
$$CON_2H_4 + 2H_2O = (NH_4)_2CO_3 \quad . \quad . \quad . \quad . \quad (2)$$

No cyanate could be detected among the products of this hydrolysis, even by the delicate copper pyridine test (Werner, J., 1923, **123**, 2577). In this respect, the hydrolysis differed from that of free guanidine, where guanidine cyanate accumulated to a considerable degree. However, it was shown (Bell, *loc. cit.*) that guanidine cyanate is also decomposed on further boiling, and since this salt would be formed at a much slower rate in the hydrolysis of the carbonate, its accumulation would be prevented by the fact that its rate of decomposition exceeds that of its formation.

The results in Table I were obtained after boiling a $N/10$-aqueous solution of guanidine carbonate under reflux for various times.

TABLE I.

	Duration of boiling.			
	1 hr.	3 hrs.	6 hrs.	12 hrs.
Urea present *	25·0	25·2	22·7	20·5
Urea converted into $(NH_4)_2CO_3$ *	0·1	11·3	16·5	22·5
Guanidine carbonate unchanged	75·0	62·7	60·9	58·0
Total (%)	100·1	99·2	100·1	101·0

* *Estimated as percentage of original guanidine carbonate in accordance with equations (1) and (2).*

The rate of hydrolysis diminishes very much after 3 hours' boiling and the reaction appears to stop after 12 hours. This retardation is due to the accumulation of ammonium carbonate in the solution (see Table II).

TABLE II.

	Expt. I.	Expt. II.	Expt. III.
Urea present	25·2	5·6	39·5
Urea converted into $(NH_4)_2CO_3$	11·3	0·0	16·5*
Guanidine carbonate unchanged	62·7	94·7	44·0
Total (%)	99·2	100·3	100·0

* Estimated by difference.

In Experiment I an $N/10$-solution of guanidine carbonate was boiled for 3 hours under reflux. In Experiment II an $N/10$-solution of guanidine carbonate, to which ammonium carbonate equivalent to 5·2 c.c. of N-acid per 100 c.c. of solution had been added, was treated in the same way. In Experiment III an $N/10$-solution of guanidine carbonate was boiled in an open flask for the same length of time, the volume being maintained constant by the addition of water to replace the loss due to evaporation. Under these conditions, ammonium carbonate volatilised as it was formed. The results of Experiment II show that the presence of ammonium carbonate checks the rate of hydrolysis very considerably, and in Experiment III, where the ammonium carbonate was allowed to escape, the change was much greater than in Experiment I.

Ammonium carbonate in solution dissociates into ammonia and carbonic acid and would therefore diminish the dissociation of guanidine carbonate into free guanidine and carbonic acid. This suggests that the hydrolysis of guanidine carbonate in aqueous solution is due to its dissociation into free guanidine and carbonic acid, the free base being hydrolysed in the manner already described. Salts of guanidine, such as the chloride, which undergo no such dissociation in aqueous solution, remain unchanged on boiling.

The ready hydrolysis of guanidine carbonate should not be overlooked in the use of this substance in the preparation of standard acid solutions.

EXPERIMENTAL.

In each experiment involving boiling, 100 c.c. of solution were used. Ten minutes were required to raise the solution to the boiling point and the burner was always adjusted to secure quiet ebullition only.

Urea was estimated by the xanthhydrol method (Fosse, *Compt. rend.*, 1913, **157**, 948). An aliquot part of the liquid was neutralised and evaporated to dryness, and the residue extracted with glacial acetic acid to which one-fourth its volume of water had been added. An excess of xanthhydrol, dissolved in methyl alcohol, was then added and after 12 hours the precipitate of dixanthylurea was collected, washed with alcohol, dried, and weighed. A small correction was applied for the slight solubility of dixanthylurea in the mixture of acetic acid, water, and methyl alcohol, the value of this correction being determined in preliminary control experiments.

The amount of urea converted into ammonium carbonate was determined by the increase in alkalinity after boiling, equation representing the only reaction producing such an increase. This necessitated the estimation, by absorption in a measured volume of standard acid, of any ammonia which escaped through the ref

condenser. In Experiment III, however, where this procedure was not possible, the change had to be estimated by difference.

Unchanged guanidine carbonate was estimated by warming gently an aliquot portion of the liquid until all ammonium carbonate was driven off, and then titrating the residue with standard acid. Control experiments showed that guanidine carbonate underwent no change during this procedure.

The author gratefully acknowledges his indebtedness to Professor E. A. Werner for advice received.

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Dublin. [*Received, June 4th*, 1928.]

CCLXXII.—*Styrylpyrylium Salts. Part X. Anhydro-pyrylium Bases and* spiro*Pyrans derived from Dibenzyl Ketone.*

By Robert Dickinson, Isidor Morris Heilbron, and Florence O'Brien.

In Part IX of this series (Dickinson and Heilbron, J., 1927, 1699) mention was made of two compounds obtained by the condensation of dibenzyl ketone with 2-naphthol-1-aldehyde. A full investigation of these substances, together with those obtained from salicylaldehyde with the same ketone, has now been made. Dilthey and Wübken (*Ber.*, 1928, **61**, 963) have also recently prepared the compounds obtained from naphtholaldehyde, without, however, studying the reactions in detail.

In the presence of piperidine, salicylaldehyde and dibenzyl ketone readily condense to give *2-hydroxy-α-phenylstyryl benzyl ketone*, $HO{\cdot}C_6H_4{\cdot}CH{:}CPh{\cdot}CO{\cdot}CH_2Ph$ (I), the constitution of which has been confirmed by the preparation of its *semicarbazone* and its *methyl ether*.

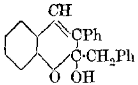
Hertzka (*Monatsh.*, 1905, **26**, 227) has previously attempted the condensation by hydrogen chloride, but failed to obtain any crystalline product. We now find this condensation to be abnormal in that pyrylium salts are only formed with difficulty and are not capable of isolation as the chlorides. From the reaction mixture two crystalline compounds have been obtained. One of these (m. p. 115°) gives analyses in agreement with the formula $C_{22}H_{16}O$ and hence is formed according to the equation :

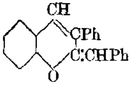
$$HO{\cdot}C_6H_4{\cdot}CHO + (CH_2Ph)_2CO = C_{22}H_{16}O + 2H_2O.$$

Probably the labile pyrylium chloride hydrolyses to the carbinol

base (II), which then loses water, yielding *2-benzylidene-3-phenyl-Δ^3-benzopyran* (III).

(II.)



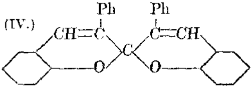


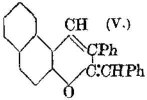
(III.)

This view is supported by its ready formation by the action of hydrogen chloride on 2-hydroxy-α-phenylstyryl benzyl ketone (I).

The other substance isolated together with (III), but only obtained in small amount, is 3 : 3′-*diphenyldibenzo*spiro*pyran* (IV). It

(IV.)





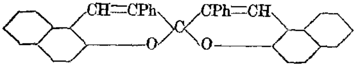
(V.)

is readily obtained as the sole product by (*a*) condensing two molecules of salicylaldehyde with one of dibenzyl ketone, (*b*) from an equimolecular mixture of salicylaldehyde and 2-hydroxy-α-phenylstyryl benzyl ketone (I), or (*c*) from the benzylidenepyran (III) and salicylaldehyde, all by the action of hydrogen chloride. We have been unable to isolate the corresponding styrylpyrylium chloride which is undoubtedly present in the solution as evidenced by the intense purplish-red colour which develops on standing. Thus dibenzyl ketone to a certain extent resembles dipropyl ketone which, according to Decker and Fellenberg (*Annalen*, 1909, **364**, 30), yields diethyl*spiro*pyran when condensed with salicylaldehyde, although the pyrylium salt may also be obtained. Other examples are 3 : 4-diphenyl-Δ^3-pentenone and 2-indanone, both of which condense with salicylaldehyde and with 2-naphthol-1-aldehyde to give *spiro*pyrans directly (Ruhemann and Levy, J., 1913, **103**, 551).

The condensation of dibenzyl ketone with 2-naphthol-1-aldehyde was again abnormal. These compounds in equivalent proportion, when treated with piperidine, failed to yield the anticipated unsaturated ketone analogous to (I), 2-benzylidene-3-phenyl-Δ^3-β-naphthapyran (V) alone being isolated. It thus appears that the naphthalene nucleus has a profound influence on the reaction, facilitating the ring closure from the enolic form of the unsaturated ketone. This compound is formed as main product when hydrogen chloride is employed and has also been prepared by Dilthey and Wübken (*loc. cit.*) by boiling the unstable pyrylium perchlorate with alcohol.

In the above acid condensation a small quantity of 3 : 3′-diphenyldi-β-naphtha*spiro*pyran (VI) is also formed. It is obtained

in better yield by treatment of a *mixture* of dibenzyl ketone and two molecules of naphtholaldehyde with hydrogen chloride, although the benzylidenepyran is still formed to some extent. As crystallised

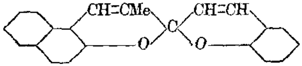


(VI.)

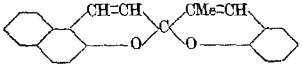
from acetone (Dickinson and Heilbron, *loc. cit.*) it gave the analytical results of a *monohydrate* and was not at first recognised as a *spiro*pyran. We have since obtained the anhydrous *spiro*pyran, which agrees in properties with that prepared by Dilthey and Wübken (*loc. cit.*), who employed a similar method.

spiro*Pyrans and Ionisation.*—From a further study of certain *spiro*pyrans, Dilthey and Wübken (*loc. cit.*) draw a parallel between the ease with which these undergo salt formation in the presence of acids (forming styrylpyrylium salts) and the ease with which they change colour on heating in inert solvents. They regard the two changes as analogous. Their arguments are based, however, almost entirely on the behaviour of 3 : 3′-trimethylenedi-β-naphtha-*spiro*pyran. Although, as shown in Part IX, this compound gives no colour in xylene, Dilthey and Wübken find that if it is heated to a sufficiently high temperature (*e.g.*, in diphenyl ether, b. p. 250°) a faint colour is developed. The compound dissolves in glacial acetic acid to a colourless solution (no salt formation), whereas in trichloroacetic acid the colour is violet.

From the above point of view, we have again examined the behaviour of the two compounds 3′- and 3-methylbenzo-β-naphtha-*spiro*pyrans (VII and VIII).



(VII.)



(VIII.)

The former, heated in diphenyl ether, undergoes *no colour change*, whereas (VIII) develops the usual wine-red colour. On the other hand, both dissolve in glacial acetic acid with salt formation to give respectively bright red and purplish-bluo solutions strictly analogous in colour to the corresponding styrylpyrylium chloride solutions. Judged from the intensity of the colour, the extent of salt formation appears to be of the same order of magnitude in each case. On Dilthey and Wübken's view, both would be expected to develop

colours in diphenyl ether. Their failure to do so shows that the case of formation of the ionic anhydro-base is not strictly comparable with salt formation. We still regard the power to "chelate" as the main factor in the production of the ionised molecule, but certainly do not dispute the possibility of ionisation effects in its absence. Generally, however, the process will require much more drastic energy conditions.

EXPERIMENTAL.

2-Hydroxy-α-phenylstyryl Benzyl Ketone (I).—A solution of dibenzyl ketone (20 g.) and salicylaldehyde (11·6 g.) in alcohol (30 c.c.) was treated with piperidine (25 drops). The yellowish-orange solution was kept at room temperature, a few drops of piperidine being periodically added, until crystallisation commenced. In subsequent preparations the time of reaction was considerably reduced by seeding the mixture. Several successive crops were obtained (total yield, 18 g.). The compound was recrystallised four times from methyl alcohol and formed pale yellow, rhombic crystals, m. p. 177°. Treated with dilute aqueous sodium hydroxide, the crystals are coloured orange-red, and a small portion dissolves to an orange solution. The compound is soluble in concentrated sulphuric acid to an orange-red solution. Although it decolorises bromine, no dibromide could be isolated (Found : C, 84·3; H, 5·9. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·7%).

The *semicarbazone*, prepared in the usual way, crystallised from alcohol in faintly yellow, glistening, rhombic plates, m. p. 196° (Found : N, 11·1. $C_{23}H_{21}O_2N_3$ requires N, 11·2%).

2-Methoxy-α-phenylstyryl benzyl ketone was readily prepared in good yield by treating an aqueous acetone solution of 2-hydroxy-α-phenylstyryl benzyl ketone with alternate small amounts of aqueous sodium hydroxide and methyl sulphate, the mixture being maintained at about 50° and continuously shaken, until no further orange colour developed with more alkali. After dilution with water, the separated solid was crystallised first from alcohol and then from acetone by addition of water, forming faintly yellow needles, m. p. 140—141° (Found : C, 84·1; H, 6·2. $C_{23}H_{20}O_2$ requires C, 84·1 : H, 6·1%).

2-Benzylidene-3-phenyl-Δ^3-benzopyran (III).—A solution of an equimolecular mixture of dibenzyl ketone (5 g.) and salicylaldehyde (2·9 g.) in alcohol (50 c.c.) was cooled in a freezing mixture and treated with a slow stream of dry hydrogen chloride until saturated; the colour changed from yellow to dark reddish-brown. After standing over-night at 0°, the mixture was poured into water and treated with aqueous sodium carbonate until faintly alkaline. The

resulting brown precipitate was dried and crystallised first from ether and then twice from alcohol, the pyran separating in glistening golden-yellow *needles*, m. p. 115° (yield, 5·5 g.). The ethereal mother-liquor yielded a small amount (0·5 g.) of the *spiro*pyran.

The benzylidene-pyran is insoluble in water and alkali, sparingly soluble in cold alcohol, readily in hot, and dissolves in concentrated sulphuric acid to a pale lemon-yellow solution. It decolorises bromine, but no product could be isolated. It is also very resistant to hydrolysis, being recovered unchanged after refluxing for 30 hours with an excess of alcoholic sodium ethoxide [Found: C, 88·9; H, 5·5; *M* (Menzies' method, in chloroform), 317. $C_{22}H_{16}O$ requires C, 89·2; H, 5·4%; *M*, 296]. Alternatively, the benzylidene-pyran may be prepared by saturating a solution of 2-hydroxy-α-phenylstyryl benzyl ketone (1 g.) in alcohol (30 c.c.) with hydrogen chloride.

3 : 3′-*Diphenyldibenzo*spiro*pyran* (IV).—A solution of dibenzyl ketone (5 g.) and salicylaldehyde (5·8 g.; 2 equivs.) in alcohol (50 c.c.) was cooled in ice-water while being saturated with dry hydrogen chloride. After several hours, the separated solid was filtered off. The filtrate, initially reddish-brown, slowly assumed an intense purplish-red colour and deposited more solid. The combined product, obtained in good yield, was crystallised first from alcohol and then twice from acetone, forming colourless needles, m. p. 197°, identical with the substance obtained as a by-product in the preparation of (III). The spiro*pyran* is insoluble in water and aqueous alkali and only sparingly soluble in alcohol. The last solution, treated with dry hydrogen chloride, slowly develops the red pyrylium colour, but from the intensity of the colour only a small amount of salt is present. In concentrated sulphuric acid, the compound dissolves to a deep red solution (Found: C, 86·8; H, 5·1; *M*, 426. $C_{29}H_{20}O_2$ requires C, 87·0; H, 5·0%; *M*, 400). When it is heated in diphenyl ether, no colour develops.

Alternatively, this *spiro*pyran may be obtained in good yield by saturating a mixture of 2-hydroxy-α-phenylstyryl benzyl ketone (1 g.) and salicylaldehyde (0·4 g.) in alcohol (30 c.c.) with hydrogen chloride, and after some hours pouring the product into water and extracting the *spiro*pyran with ether.

2-*Benzylidene*-3-*phenyl*-Δ^3-β-*naphthapyran* (V).—Equimolecular quantities of 2-naphthol-1-aldehyde (2·5 g.) and dibenzyl ketone (3·5 g.), dissolved in alcohol (45 c.c.), were treated with a few drops of piperidine and heated on the water-bath under reflux for 8 hours. After cooling, the crystalline deposit was recrystallised twice from acetone, separating in brilliant reddish-orange needles, m. p. 145°.

This pyran is insoluble in alkali, but dissolves in concentrated sulphuric acid to a *lemon-yellow solution which shows an intense bright green fluorescence* (Found: C, 89·6; H, 5·3; *M*, 360. Calc. for $C_{26}H_{18}O$: C, 90·1; H, 5·2%; *M*, 346).

The same compound was obtained in better yield by saturating a solution of dibenzyl ketone (5 g.) and 2-naphthol-1-aldehyde (4·1 g.) in alcohol (40 c.c.) with hydrogen chloride, the mixture being cooled in ice-water. After being kept in the ice-chest for 12 hours, the reddish-brown solution was poured into water and extracted with ether. The extract, dried and concentrated, *deposited orange needles (4·5 g.) which, recrystallised from acetone,* proved to be identical with the pyran described above (m. p. 145°). The ethereal mother-liquor yielded a small amount of the *spiro*pyran.

On being kept for several days in acetone solution, the benzylidene-pyran undergoes a peculiar change; the orange colour disappears and a pale yellow, amorphous solid (m. p. above 200°), which has resisted all attempts at crystallisation, separates. The change does *not seem to occur in any solvent other than acetone.*

3 : 3′-*Diphenyldi-β-naphtha*spiro*pyran* (VI).—A mixture of 2-naphthol-1-aldehyde (5 g.) and dibenzyl ketone (3·5 g.) was dissolved in alcohol (40 c.c.), saturated with hydrogen chloride, and kept over-night in the ice-chest. The reddish-brown solution was slowly poured into water, and the resulting curdy brown solid filtered off and well washed. After drying in a vacuum, it was fractionally crystallised from acetone. The main product (2·5 g.) was finally obtained in almost colourless needles, m. p. 248°; the *analysis was that of the monohydrate of the spiropyran (Found:* C, 85·4; H, 5·3. $C_{37}H_{24}O_2,H_2O$ requires C, 85·7; H, 5·0%). The anhydrous compound may be obtained by recrystallisation from benzene with the addition of light petroleum, and has the same m. p. as the hydrate (Found: C, 89·4; H, 5·3. Calc. for $C_{37}H_{24}O_2$: C, 88·8; H, 4·8%).

The *spiro*pyran is practically insoluble in alcohol, only sparingly soluble in acetone, and fairly readily soluble in benzene. It dissolves in concentrated sulphuric acid to a dark red solution, which develops a dark green fluorescence after several hours. No colour develops when it is heated in solvents, such as diphenyl ether.

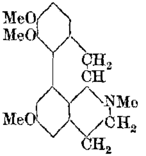
THE UNIVERSITY, LIVERPOOL. [*Received, June 2nd*, 1928.]

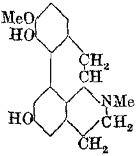
CCLXXIII.—*Synthetical Experiments on the Aporphine Alkaloids. Part IV. A Synthesis of Morphothebaine Dimethyl Ether.*

By John Masson Gulland and Robert Downs Haworth.

The method for the preparation of bases of the aporphine group which was described in Part I of this series (this vol., p. 581) has now been extended to the synthesis of 3 : 4 : 6-*trimethoxyaporphine* (I). The lævo-form of this base is identical with morphothebaine dimethyl ether (Klee, *Arch. Pharm.*, 1914, **252**, 242), and thus the structure for morphothebaine (II) advanced by Pschorr and Halle (*Ber.*, 1907, **40**, 2004) is substantiated. Morphothebaine is produced when hot concentrated hydrochloric acid acts on thebaine, and as a phenanthreno*iso*quinoline base, it forms one of the connecting links between the morphine and aporphine groups of alkaloids.

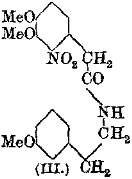
(I.)



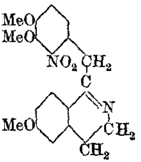


(II.)

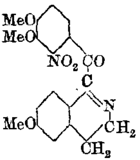
2′-*Nitro*-3′ : 4′-*dimethoxyphenylaceto*-β-3-*methoxyphenylethylamide* (III), prepared by the interaction of 2-nitro-3 : 4-dimethoxyphenylacetyl chloride and 3-methoxy-β-phenylethylamine (Helfer, *Helv. Chim. Acta*, 1924, 7, 945), was converted into 2′-*nitro*-6 : 3′ : 4′-*trimethoxy*-1-*benzyl*-3 : 4-*dihydro*isoquinoline (IV) by the action of phosphorus pentachloride. This pale yellow crystalline base, which forms a sparingly soluble *hydrochloride*, *sulphate*, and *methiodide*,



(III.)



(IV.)



(V.)

is remarkably stable to atmospheric oxidation, but a small quantity of feebly basic 2′-*nitro*-6 : 3′ : 4′-*trimethoxy*-1-*benzoyl*-3 : 4-*dihydro*-

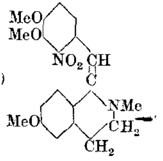
isoquinoline (V) was actually isolated from the mother-liquor of the preparation of the base (IV), and was converted into the amorphous, alkali-soluble *oxime*.

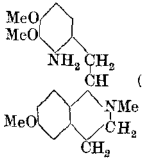
The methiodide of the base (IV), which was abnormal in that it did not appear to undergo alkaline scission but yielded only the crystalline anhydro-base, *2'-nitro-6 : 3' : 4'-trimethoxy-1-benzylidene-2-methyltetrahydro*iso*quinoline* (VI), was reduced with zinc dust and hydrochloric acid to *2'-amino-6 : 3' : 4'-trimethoxy-1-benzyl-2-methyltetrahydro*iso*quinoline* (VII), an oily base which yielded a crystalline *dihydrochloride* and diazotised readily. The base (VII) was diazotised in a mixture of methyl alcohol and sulphuric acid, and converted by heating into *3 : 4 : 6-trimethoxyaporphine* (I), an oil from which a crystalline *hydriodide* has been prepared.

This *dl*-base (I) was resolved by means of *d*-tartaric acid, and *l*-morphothebaine dimethyl ether hydrogen *d*-tartrate obtained in crystalline condition. It appeared from its crystalline form melting point, and rotation, and by a mixed melting-point determination, to be identical with the salt prepared from morphothebaine in the manner described by Klee (*loc. cit.*). The *l*-base was obtained from the hydrogen tartrate as an uncrystallisable oil, which showed the same colour reactions and rotation as a specimen of natural morphothebaine dimethyl ether. Further, the *methiodides* of the two preparations appeared from a comparison of their crystalline form, melting point, and rotations to be similar in every respect and there can be no doubt that the synthetical and natural product are identical.

d-Morphothebaine dimethyl ether hydrogen l-tartrate was obtained from the mother-liquor of the resolution by liberating the crude *d*-base and allowing it to combine with *l*-tartaric acid. The *d*-base is an oil which has not crystallised.

(VI.)





(VII.)

Experimental.

2'-Nitro-3' : 4'-dimethoxyphenylaceto-β-3-methoxyphenylethylamide (III).—2-Nitro-3 : 4-dimethoxyphenylacetyl chloride (from 10 g of acid) in benzene (50 c.c.) was added gradually to a solution o

3-methoxy-β-phenylethylamine (7 g.) in benzene (50 c.c.). After a short time, the dull yellow precipitate which had separated was mixed with 8% sodium hydroxide solution, and the benzene layer was washed with water and dried. When the solvent had been removed, the residual brown oil solidified; it was then crystallised from methyl alcohol, from which the *amide* separated in colourless needles, m. p. 107—108° (Found: C, 60·7; H, 5·9. $C_{19}H_{22}O_6N_2$ requires C, 61·0; H, 5·9%).

*2′-Nitro-6 : 3′ : 4′-trimethoxy-1-benzyl-3 : 4-dihydro*iso*quinoline* (IV).—A solution of the amide (III) (10 g.) and phosphorus pentachloride (12 g.) in chloroform (80 c.c.) was kept at room temperature for 36 hours. After the solvent and phosphorus oxychloride had been removed from the mass of felted needles by distillation under reduced pressure, the residue was dissolved in boiling water, and the solution was filtered and cooled. The sparingly soluble *hydrochloride* of the base (IV) which separated was collected (see below for examination of the mother-liquor), suspended in hot water, and decomposed by ammonia. The *base* (IV) thus liberated crystallised from methyl alcohol in faintly yellow, blunt-ended prisms, m. p. 121—123° (7·5 g.) (Found: C, 64·2; H, 5·5. $C_{19}H_{20}O_5N_2$ requires C, 64·0; H, 5·6%).

The *hydrochloride* separated in colourless needles, m. p. 217—218° (decomp.), when a solution of the base in hot dilute hydrochloric acid was cooled (Found: Cl, 9·0. $C_{19}H_{20}O_5N_2$,HCl requires Cl, 9·0%). It is moderately easily soluble in water and ethyl alcohol, but very sparingly soluble in dilute hydrochloric acid. The *sulphate*, prepared by dissolving the base in dilute sulphuric acid, forms colourless needles, m. p. 237° (decomp.).

The *methiodide* was obtained in a yield exceeding 90% when a mixture of the base and an excess of methyl iodide was heated under reflux on the water-bath for 30 minutes, and the excess of methyl iodide removed. It crystallised from ethyl alcohol in yellow needles, m. p. 220° (decomp.), which were sparingly soluble in water (Found: C, 48·4; H, 4·9. $C_{20}H_{23}O_5N_2I$ requires C, 48·2; H, 4·6%). This substance appeared to be unusually stable to alkaline fission, and attempts to decompose it with sodium hydroxide of various concentrations led only to *2′-nitro-6 : 3′ : 4′-trimethoxy-1-benzylidene-2-methyltetrahydro*iso*quinoline* (VI), which separated as a red oil and was extracted with benzene. When the solution was dried and the solvent removed, the base (VI) solidified; after twice crystallising from benzene–ligroin, it was obtained in prisms, m. p. 108—109°, which appeared as red diamond-shaped tablets or as yellow prisms, according to the angle from which they were observed (Found in material dried at 100°: C, 64·9; H, 6·0. $C_{20}H_{22}O_5N_2$ requires

C, 64·9; H, 5·9%). By adding sodium iodide to a solution of the base (VI) in dilute hydrochloric acid, the *methiodide* of the base (IV) was regenerated as an oil which crystallised when rubbed with ethyl alcohol.

*2'-Nitro-6 : 3' : 4'-trimethoxy-1-benzoyl-3 : 4-dihydro*iso*quinoline* (V).—The acid mother-liquor from which the hydrochloride of the base (IV) had separated (see above) was rendered alkaline with ammonia: the precipitate obtained, when crystallised twice from methyl alcohol, formed faintly yellow prisms, m. p. 164° (decomp.) (Found: C, 61·5; H, 4·9; N, 7·5. $C_{19}H_{18}O_6N_2$ requires C, 61·6; H, 4·9; N, 7·5%). This substance is insoluble in alkali, but dissolves in warm dilute hydrochloric acid and is reprecipitated by sodium acetate. A consideration of its properties leads us to assign to it the constitution (V), and in this connexion it is noteworthy that the colour of a solution of the compound in boiling acetic anhydride is yellow, whereas the non-nitrated 1-benzoyl-3 : 4-dihydro*iso*quinolines develop a characteristic green coloration under the same conditions (Buck, Haworth, and Perkin, J., 1924, **125**, 2176). The *oxime*, prepared by the action of hydroxylamine hydrochloride and pyridine at 100°, is amorphous and dissolves readily in dilute sodium hydroxide solution.

*2'-Amino-6 : 3' : 4'-trimethoxy-1-benzyl-2-methyltetrahydro*iso*quinoline* (VII).—The methiodide (8 g.) of the base (IV), suspended in water (80 c.c.) and concentrated hydrochloric acid (150 c.c.), was heated on the water-bath and reduced by the gradual addition of zinc dust (31 g.). The clear, colourless solution was then cooled, and on several occasions a zinc chloride double salt separated in characteristic, colourless, fan-shaped aggregates of needles. After the addition of an excess of sodium hydroxide solution, the base was isolated by repeated extraction with ether; this extract, when washed with water, dried, and distilled, yielded a pale yellow, uncrystallisable oil. This was converted into its *dihydrochloride* by treating an absolute alcoholic solution with dry hydrogen chloride and evaporating the solution to dryness under reduced pressure. The residual oil crystallised from dry chloroform in colourless needles which softened and shrank at 135°, melted at 155°, and retained solvent when dried in a vacuum desiccator (Found in material dried in a vacuum desiccator: Cl, 32·0. $C_{20}H_{26}O_3N_2,2HCl,CHCl_3$ requires Cl, 33·2%). This substance diazotises readily, and the diazonium salts couple with β-naphthol in alkaline solution, yielding a scarlet dye which develops a reddish-purple colour with concentrated sulphuric acid.

dl-*3 : 4 : 6-Trimethoxyaporphine* (I).—A solution of the hydrochloride of the base (VII) (5 g.) in 2*N*-sulphuric acid (30 c.c.) was

boiled in order to free it from chloroform, cooled in ice, and diazotised by the calculated amount of 2*N*-sodium nitrite. After the addition of methyl alcohol (30 c.c.), the orange solution was boiled under reflux for 30 minutes, mixed with concentrated hydrochloric acid (6 c.c.), reduced by zinc dust (2 g.), cooled, filtered, and made alkaline with 30% sodium hydroxide solution. The base (I) was isolated as a pale yellow oil by repeated extraction with ether, followed by the removal of the solvent, and was converted into the *hydriodide* by the addition of sodium iodide to a solution in dilute hydrochloric acid. This salt separated as a gum, but crystallised when rubbed with ethyl alcohol after the mother-liquor had been decanted, and when recrystallised from the same solvent formed almost colourless needles, m. p. 227° (decomp.) (Found in material dried at 100°: C, 53·2; H, 5·2. $C_{20}H_{23}O_3N,HI$ requires C, 53·0; H, 5·3%). It is sparingly soluble in water and separates as a granular, non-crystalline mass when a hot solution is cooled.

Resolution of dl-3 : 4 : 6-*Trimethoxyaporphine.* 1-*Morphothebaine Dimethyl Ether.*—The oily *dl*-base (I) was liberated from the hydriodide by sodium carbonate and extracted with ether, and the solvent evaporated. The residue, dissolved in a little 95% ethyl alcohol, was mixed with an alcoholic solution of an equimolecular amount of *d*-tartaric acid; in a few moments, the colourless *l*-morphothebaine dimethyl ether hydrogen *d*-tartrate separated. It crystallised from ethyl alcohol in stellate aggregates of shining needles, m. p. 208—209° (decomp.) (Found in material dried at 100°: C, 60·3; H, 6·3. Calc. for $C_{24}H_{29}O_9N$: C, 60·6; H, 6·1%). In aqueous solution, $c = 1·123$, $l = 1$, $\alpha_D = -0·84°$, whence $[\alpha]_D = -74·8°$. *l*-Morphothebaine was liberated as a colourless oil from the hydrogen tartrate (0·1684 g.) and carefully extracted by successive small quantities of chloroform, and the mixed extracts were dried with a little sodium sulphate and made up to 20 c.c.; $l = 1$, $\alpha_D = -1·00°$, whence $[\alpha]_D = -173·5°$. The colour reactions with Erdmann's and Fröhde's reagents were indistinguishable from those given by the natural *l*-base (see below). The *methiodide* separated in crystalline condition when a solution of the base and methyl iodide in ethyl acetate was warmed for a few minutes on the water-bath; it crystallised from ethyl alcohol in colourless needles which became pasty at 190° and melted at 195° (Found in material dried at 100°: C, 54·0; H, 5·6. $C_{21}H_{26}O_3NI$ requires C, 54·0; H, 5·6%). In aqueous solution, $c = 0·448$, $l = 1$, $\alpha_D = -0·39°$, whence $[\alpha]_D = -87·1°$.

Natural 1-*Morphothebaine Dimethyl Ether.*—For comparison, a specimen of natural morphothebaine dimethyl ether was prepared by methylating morphothebaine with diazomethane as described

by Klee (*loc. cit.*). The oil obtained in this way was converted int the hydrogen *d*-tartrate, which crystallised from 95% ethyl alcoh in stellate clusters of shining needles, m. p. 208—209° (decomp. (Klee gives 205°), and there was no depression of the melting poin of a mixture of this material with the synthetical product. I aqueous solution, $c = 1{\cdot}040$, $l = 1$, $\alpha_D = -0{\cdot}78°$, whence $[\alpha]_D = -75{\cdot}0°$ (Klee gives $-74{\cdot}3°$). The oily base, which was liberate by sodium carbonate solution from the hydrogen *d*-tartrate (0·215 g.), was extracted with chloroform (20 c.c.) as described in the cas of the synthetical substance; $l = 1$, $\alpha_D = -1{\cdot}27°$, whence $[\alpha]_D = -172{\cdot}7°$ (Klee gives $-184{\cdot}8°$). With Erdmann's reagent a olive-green colour was immediately developed which changed t a dirty violet-blue and then became red on dilution, and wit Fröhde's reagent a deep bluish-green colour was produced whic finally became dull violet. The methiodide, prepared as describe for the synthetical material, crystallised in needles which becam pasty at 190° and melted at 195°, and this melting poin was not altered on admixture with the synthetical preparatior In aqueous solution, $c = 0{\cdot}533$, $l = 1$, $\alpha_D = -0{\cdot}47°$, whenc $[\alpha]_D = -88{\cdot}2°$.

d-*Morphothebaine Dimethyl Ether*.—The alcoholic mother-liquo from which the *l*-morphothebaine dimethyl ether hydrogen *d*-tartrat had separated (see above) was concentrated, mixed with ammonia and extracted with ether. The extracts were washed with water dried, and distilled, and the residue was converted into d-*morpho thebaine dimethyl ether hydrogen* l-*tartrate* by mixing an alcoholi solution with an alcoholic solution of the requisite amount o *l*-tartaric acid. This salt separated when the vessel was rubbed and crystallised from ethyl alcohol in stellate clusters of shinin needles, m. p. 208—209° (decomp.) (Found in material dried at 100° C, 60·6; H, 6·3. $C_{24}H_{29}O_9N$ requires C, 60·6; H, 6·1%). I aqueous solution, $c = 0{\cdot}821$, $l = 1$, $\alpha_D = +0{\cdot}62°$, whence $[\alpha]_D = +75{\cdot}5°$. The colourless oily d-*base*, liberated from the hydroger *l*-tartrate (0·1231 g.), was dissolved in chloroform (20 c.c.); $l = 1$ $\alpha_D = +0{\cdot}76°$, whence $[\alpha]_D = +174{\cdot}2°$.

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CCLXXIV.—*The Action of Magnesium Phenyl Bromide on Methyl* o-*Cyanobenzoate.* 1 : 3-*Diphenyldihydro*-iso*indole.*

By DAVID RUNCIMAN BOYD and DONALD ERNEST LADHAMS.

IT has been shown by Haller and Legagneur (*Compt. rend.*, 1925, **180**, 1621) that magnesium methyl iodide in ethereal solution reacts with the methyl ester of camphoric acid α-mononitrile to give the corresponding cyano-tertiary alcohol :

$$CN{\cdot}C_8H_{14}{\cdot}CO_2Me \longrightarrow CN{\cdot}C_8H_{14}{\cdot}CMe_2{\cdot}OH\,;$$

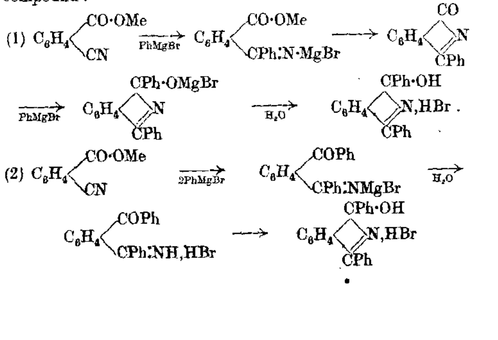
in boiling toluene solution, however, the nitrile group also is attacked, the product being the ketonic tertiary alcohol,

$$COMe{\cdot}C_8H_{14}{\cdot}CMe_2{\cdot}OH.$$

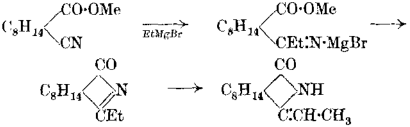
Using magnesium phenyl bromide in ethereal solution, the same authors obtained (*ibid.*, p. 881) the ketimine hydrobromide, $C_8H_{14}(COPh){\cdot}CPh{:}NH,HBr$. No observations appear to be on record with regard to the action of a Grignard reagent on an aromatic compound containing both a cyano- and a carbalkyloxy-group. It seemed possible that the cyano-group in such a compound would show a reactivity considerably less than that of the other competing group, and methyl *o*-cyanobenzoate was investigated by us in the hope of obtaining *o*-cyanotriphenylcarbinol.

We have found, however, that magnesium phenyl bromide in ethereal solution converts the ester almost quantitatively into the hydrobromide of a base which we consider to be 1-hydroxy-1 : 3-diphenyl*iso*indole. No trace of the isomeric *o*-cyanotriphenylcarbinol could be detected.

Two different routes may be suggested as leading to the *iso*indole compound :



Ring formation by elimination of MeO·MgBr, as in scheme (1), has been postulated by Salmon-Legagneur (*Ann. Chim.*, 1927, **8**, 5) to explain the formation of a nitrogen-ring compound by the action of magnesium ethyl bromide on the methyl ester of camphoric acid α-mononitrile :



In scheme (2) the *iso*indole derivative is assumed to arise from the ketimine hydrobromide by an intramolecular change.

Although the *iso*indole formula * appears to us the more probable, the isomeric ketimine constitution cannot be definitely excluded. In certain solutions both forms of the compound may be present :

(I.) (II.)

The comparative ease with which hydrolysis to *o*-dibenzoylbenzene takes place on boiling with dilute sulphuric acid may be regarded as evidence of the presence of (I) in the solution. On the other hand, the ring structure is supported by the following considerations :

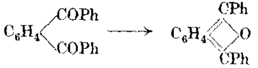
(1) With concentrated sulphuric acid the base behaves like a tertiary aromatic carbinol, giving a solution of an intense magenta colour. In this solution the compound shows great stability; heating in a water-bath for 2 hours produced little or no alteration.

(2) The base can be reduced to 1 : 3-diphenyldihydro*iso*indole :

The reduction was effected by means of zinc dust and acetic acid, and the yield was small. Most of the base was converted into a yellow solid apparently identical with diphenylbenzfuran (Guyot and Catel, *Bull. Soc. chim.*, 1906, **35**, 1124). The appearance of this substance is attributed to hydrolysis resulting in the formation of dibenzoylbenzene, which is then reduced to the benzfuran.

* Compounds related to *iso*indole have also been obtained by Weiss and co-workers (*Monatsh.*, 1924, **45**, 105; 1927, **48**, 451) by the action of Grignard reagents on *o*-phthalonitrile.

Experiment showed that reduction of dibenzoylbenzene under similar conditions leads to the same yellow product :



Efforts to improve the yield of 1 : 3-diphenyldihydro*iso*indole by the use of other reducing agents were unsuccessful.

1 : 3-Diphenyldihydro*iso*indole appears to be the first example of a 1 : 3-disubstituted dihydro*iso*indole. The parent substance and its 1-methyl derivative were described by Gabriel (*Ber.*, 1893, **26**, 526, 711, 2213), but only *N*-substituted dihydro*iso*indoles have been prepared subsequently. The compound was found to be much more stable than the unsaturated substance from which it was derived, being unattacked by boiling dilute acid or alcoholic potash, and only oxidised extremely slowly by chromic–acetic acid to dibenzoylbenzene. It behaves as a strong secondary base, giving readily crystallised salts and a *nitroso*-, a *monobenzoyl* and a p-*toluenesulphonyl* derivative (the last alkali-insoluble). From its mode of preparation it might be expected to have the *trans*-, and therefore racemic, configuration, but the material available was not sufficient for experiments on resolution.

The study of the reaction between cyanobenzoic esters and organomagnesium halides is being continued.

EXPERIMENTAL.

Methyl *o*-cyanobenzoate was prepared in 65% yield from methyl anthranilate by Clarke's modification of the Sandmeyer reaction (*J. Amer. Chem. Soc.*, 1924, **46**, 1001). The oily product was distilled under reduced pressure, b. p. 154°/15 mm., and crystallised in the receiver to colourless plates, m. p. 51°.

The Action of Magnesium Phenyl Bromide on Methyl o-*Cyanobenzoate*.—28·6 G. of the ester (1 mol.) in 300 c.c. of ether were run slowly, with constant stirring, into the ice-cold Grignard reagent prepared from 86 g. of bromobenzene (3 mols.) and 12·2 g. of magnesium (2¾ atoms) in 250 c.c. of ether. Each drop gave a yellow precipitate, so that finally a semi-solid mass was obtained. This was refluxed for an hour, cooled, and decomposed with ice and dilute sulphuric acid. The yellow solid, 1-*hydroxy*-1 : 3-*diphenyl*iso*indole hydrobromide*, was collected and washed with ether, in which it was almost insoluble. Yield, 50 g. (90%). The brown ethereal filtrate gave on evaporation a small amount of gummy material, from which unchanged ester was crystallised by rubbing with alcohol. The

hydrobromide was crystallised from chloroform–benzene, but could not be obtained pure. It decomposed above 220°. Attempts to crystallise it from alcohol converted it into *o*-dibenzoylbenzene. The free *base* was obtained by rubbing the hydrobromide with aqueous sodium carbonate, and a little ether to remove gummy matter (some decomposition occurred as shown by the evolution of ammonia). The prismatic crystals obtained from aqueous methyl or ethyl alcohol melted at 192·5° (decomp.) (Found: C, 83·7; H, 5·4; N, 4·9. $C_{20}H_{15}ON$ requires C, 84·1; H, 5·3; N, 4·9%). When boiled in alcoholic potash or dilute sulphuric acid for an hour, the base was quantitatively decomposed into *o*-dibenzoylbenzene, m. p. 145° (Found: C, 83·2; H, 5·1. Calc. for $C_{20}H_{14}O_2$: C, 83·9; H, 4·9%), ammonia also being formed. The *o*-dibenzoylbenzene was identified by conversion into the oxime, m. p. 149—150° after crystallisation from methyl alcohol. The ketone gave a colourless solution with concentrated sulphuric acid. Guyot and Catel (*loc. cit.*) record 146° and 150° as the melting points of the ketone and oxime, and state that the solution of the ketone in sulphuric acid has a pink colour.

The free base dissolved in concentrated, or slightly diluted, sulphuric acid to give a magenta-coloured solution; the hydrobromide gave off hydrogen bromide and bromine. This solution could be boiled for some minutes or heated in the water-bath for 2 hours without any marked decomposition, as shown by cooling, pouring on ice, filtering off any traces of dibenzoylbenzene and neutralising the filtrate. An attempt was made to condense the hydroxy*iso*indole with phenol in the presence of sulphuric acid (Baeyer and Villiger, *Ber.*, 1902, **35**, 3018; Boyd and Hardy, this vol., p. 630). Sulphonation occurred, however, and the product was an amphoteric uncrystallisable substance.

With a view to obtaining evidence as to the constitution of the product arising in the Grignard reaction, experiments on benzoylation were carried out. Before decomposition of the Grignard complex with ice, benzoyl chloride (1 mol.) was run slowly into the well-cooled suspension, which was then refluxed for an hour, cooled, and treated with ice and ammonium chloride. A small quantity of solid remained, insoluble in the ether layer; this was extracted with alcohol, which deposited on dilution a colourless solid, m. p. 220°, containing nitrogen but giving no coloration with concentrated sulphuric acid (Found: C, 84·3; H, 5·6; N, 4·4. $C_{20}H_{15}ON$ requires C, 84·1; H, 5·3; N, 4·9%). On repeating the experiment this substance was not obtained, so that further investigation was not possible. The ethereal solution in each case contained dibenzoylbenzene, benzamide, and tarry matter.

Reduction of 1-*Hydroxy*-1 : 3-*diphenylisoindole*.—An acetic acid solution of the base was kept with excess of zinc dust for 2 days, with occasional warming. The filtrate exhibited a blue fluorescence (destroyed by exposure to light and air), and gave on dilution a deep-yellow solid. This could not be satisfactorily crystallised, but its m. p. of 120—125°, its oxidation by chromic-acetic acid to dibenzoylbenzene, and its behaviour in solution point to its identity with Guyot and Catel's diphenylbenzfuran, m. p. 125°. Dibenzoylbenzene was reduced under the same conditions to the same substance. The diluted acetic acid filtrate gave on neutralisation a white precipitate of 1 : 3-*diphenyldihydroisoindole* in very poor yield. The yield was increased to about 10 to 20% by adding the hydrobromide in small quantities to the boiling suspension of zinc dust in acetic acid. The colourless prisms from alcohol melted at 109° (*Found*: C, 87·95; H, 6·55; N, 5·1. $C_{20}H_{17}N$ *requires* C, 88·45; H, 6·3; N, 5·2%). The base is soluble in the usual organic solvents, and in dilute mineral acids; the solution in hot dilute hydrochloric acid gave crystals of the *hydrochloride* on cooling, m. p. 270—280° (decomp.) (Found: Cl, 11·36. $C_{20}H_{17}N,HCl$ requires Cl, 11·53%). The base was slowly oxidised by gradually adding a slight excess of chromic anhydride to an acetic acid solution heated in a waterbath. On cooling, dibenzoylbenzene crystallised.

On adding aqueous sodium nitrite to a dilute sulphuric acid solution of the base, a white precipitate of the *nitroso*-derivative, $C_6H_4(CHPh)_2N{\cdot}NO$, slowly formed. The crystals from alcohol were pinkish, but yellow while in the steam-oven, and melted at 175—175·5° (Found: N, 9·5. $C_{20}H_{16}ON_2$ requires N, 9·3%). This substance was unaffected by alcoholic hydrochloric acid, and could not be reduced to the corresponding hydrazine by zinc dust in acetic acid. On applying Liebermann's test it gave a green solution in the sulphuric acid–phenol mixture. The *benzoyl* derivative (Schotten–Baumann method) gave crystals very sparingly soluble in alcohol, m. p. 236° (Found: N, 3·9. $C_{27}H_{21}ON$ requires N, 3·7%). On treatment with phosphorus pentachloride (v. Braun, *Ber.*, 1904, **37**, 2818) it gave an intractable tarry material. The p-*toluenesulphonyl* derivative melted at about 255° (decomp.). It was insoluble in alkali.

One of us (D. E. L.) wishes to thank the Department of Scientific and Industrial Research for a grant which enabled him to take part in this investigation.

UNIVERSITY COLLEGE, SOUTHAMPTON. [*Received, June 13th, 1928.*]

CCLXXV.—*Striated Photographic Records of Explosion Waves. Part II. An Explanation of the Striæ.*

By Colin Campbell and Arthur Calvert Finch.

It has been shown (J., 1926, 3010; 1927, 1572) that when the explosion-wave in certain gaseous mixtures is photographed by means of a moving-film camera, the records are striated in appearance and the trace of the flame front is marked by regular undulations. The mixtures which showed these phenomena most clearly were those of carbon monoxide and oxygen, with or without the addition of small quantities of hydrogen. The period of the striæ and also of the undulations was approximately proportional to the diameter of the containing tube but independent of its length. In a tube of internal diameter 15 mm. the period was about 1/39,000 sec. and was apparently not affected by the method of ignition of the gases. Several suggestions were put forward as to the cause of these phenomena, such as induced vibrations in the apparatus, a periodic propagation of the explosion-wave, or (as suggested by Mr. E. F. Greig) the flame travelling along a helical path.

The experiments now recorded appear to show that the facts can be accounted for by the last suggestion, and that the vibration of the apparatus or of a column of the gaseous mixture is not responsible for the effect.

Experimental.

The general experimental procedure previously described (J., 1926, 3010) has again been used except that, since only one gaseous mixture was under observation in any one experiment, the diaphragm apparatus was no longer necessary. The explosion apparatus consisted simply of glass and lead tubes of the same internal diameter (usually 12·5 or 15 mm.) rigidly cemented together to form a continuous gallery, usually about 4 m. long, which was placed horizontally in front of a moving-film camera. The explosive mixture was ignited by a break-spark near the closed end of the gallery, the other end (often seen in the photographs) being opened just before firing. The photographs were obtained on Lumière paper, usually 100 mm. wide, which was fastened to a cylindrical drum capable of being rotated at peripheral speeds up to 55 m. per sec. In order to obtain the exact direction of movement of the film as it passed the focus of the camera lens, a small electric lamp, placed near the tube and giving a pin-hole illumination, was lit for several seconds just before the mixture was ignited: this produced the thin black lines seen on many of the photographs.

The "Vibration" Theory.

It was at first imagined that the striæ might have been caused by the vibration of the camera itself, but the fact already mentioned (J., 1927, 1576), that striæ of different periods in two portions of the same tube have been recorded together on the same film, would appear to disprove such an explanation. Further evidence against it can now be given. For example, *striæ of gradually increasing* periods were obtained when a conical, instead of a cylindrical tube was employed. This is shown in Fig. 1, which was obtained when the internal diameter of the tube increased from 10 mm., on the right, to 25 mm., on the left of the photograph. An *abrupt* change in the internal diameter of the explosion tube has a marked effect on the speed of the flame as well as on its general character (Campbell, J., 1922, **121**, 2483), but the gradual widening of the tube produced no alteration in the speed of the flame in this experiment. In two experiments where the widening was more rapid (the diameter increased from 15 mm. to 28 mm. over a distance of 31 cm.), the character of the flame was altered and its speed reduced.

Vibration of the camera being excluded, that of the explosion tube was next examined. Such vibrations, set up by the explosion itself or transmitted through the bench from the driving motor on the concrete floor, might be either (1) longitudinal vibrations similar to those in a freely supported bar after a sharp knock, or (2) transverse vibrations in the material of the tube (compare vibrations of a bell) causing alternate compression and rarefaction of the hot gases.

Longitudinal vibrations in a glass tube would have a frequency proportional to its length; they would have the same frequency in all parts of the same tube and would almost certainly show the presence of nodes and anti-nodes at fixed points in it. The striæ, however, have a frequency which is independent of the length of the tube, the frequency is not always the same in different parts of the same tube (*e.g.*, in a conical tube), and the undulations on the trace of the wave-front do not correspond to the same points in the tube in different experiments. Moreover, the frequency of the striæ in one particular tube is about 40,000 per second, whereas the fundamental frequency of the longitudinal vibrations of this tube has been calculated to be about 2,500.

The theory that the striæ are caused by *transverse* vibrations in the material of the tube would appear to gain support from the close relationship which has been found to exist between the frequency of the striæ and the diameter of the tube. On this view, it might be expected that an alteration in the thickness of the wall of the explosion tube would alter the frequency of the striæ. This

change has not been observed, but as no method appears to be available for calculating the variation of frequency with wall thickness for bell-vibrations of this type, we are unable to predict whether the effect would be sufficiently great to be apparent. It seemed probable, however, that a change in the elastic properties of the tube wall would alter the frequency of vibration to a much greater extent, and rubber tubes might therefore be expected to give results different from those in glass; but experiments in which a section of the glass explosion tube was replaced by one made of (a) thick rubber provided with a thin glass window, and (b) very thin semi-transparent rubber, showed striæ of similar frequencies in the glass and rubber sections of the tube.

Since no difference in the striæ could be seen when tubes of rubber and glass were used, an attempt was made to reduce to a minimum any possible transverse vibrations in a glass tube. For this purpose, the glass explosion tube, instead of being clamped, was encased in a large block of cement (reinforced by iron bolts) except for a slit 3 cm. wide extending along the middle 60 cm. of its length. The photograph obtained through this slit showed striæ of the same intensity and frequency as those observed in a tube clamped in the ordinary way.

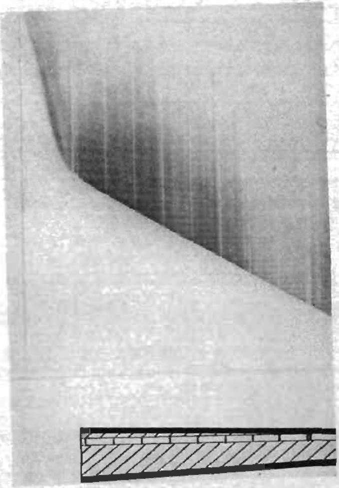
It would appear, therefore, that vibrations either longitudinal or transverse in the tube itself cannot explain the formation of the striæ.

A train of compression waves in the gaseous mixture, initiated at or near the open end of the tube and moving in a direction opposite to that of the flame motion, might produce striæ, but it has previously been pointed out (J., 1927, 1573) that the slope of the striæ actually observed would require the velocity of such waves to be almost infinitely great. In any case, it seems impossible to believe that the open end of the tube could be a region of high pressure several milliseconds before the flame had arrived there. That the method of ignition also is not concerned in the formation of the striæ is shown by the fact that their frequency is unchanged (a) when the frequency of electrical oscillations is altered by increasing the capacity of the secondary circuit, and (b) when the mixture is ignited by a taper, the tube, in this experiment, being open at both ends.

The "Helix" Theory.

If a flame is travelling along a helical path in a cylindrical tube, it should appear at two windows separated by an arc of 90° at a time interval which is one fourth of that required for consecutive appearances at the same window. To test this by viewing the flame through

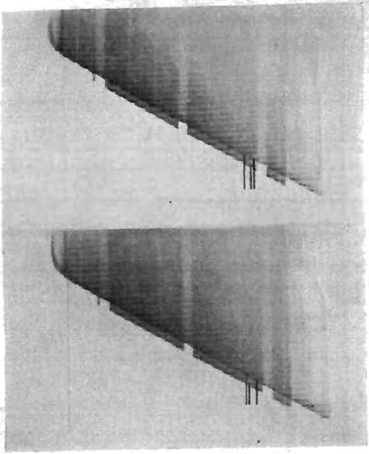
Fig. 1.



← - - - - - - - 93 cm. - - - - - - - →

[To face p. 2096.]

Fig. 2.



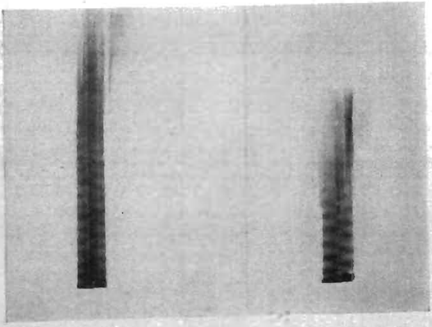
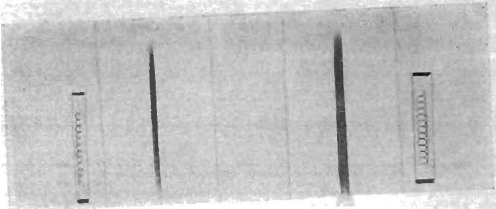


Fig. 8.

Fig. 9.

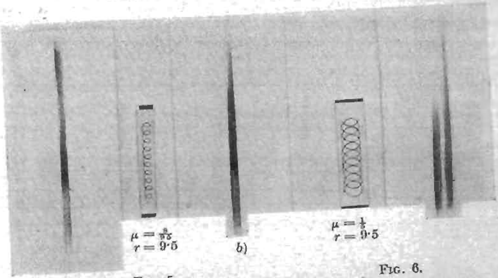


$\mu = \frac{1}{15}$
$r = 7 \cdot 5$

FIG. 3.

$\mu = \frac{2}{15}$
$r = 7 \cdot 5$

FIG. 4.

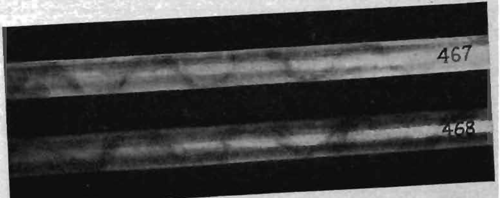


$\mu = \frac{2}{25}$
$r = 9 \cdot 5$

$\mu = \frac{1}{5}$
$r = 9 \cdot 5$

(a) FIG. 5. b)

FIG. 6.



⟵ *Direction of propagation of explosion-wave.*

FIG. 7.

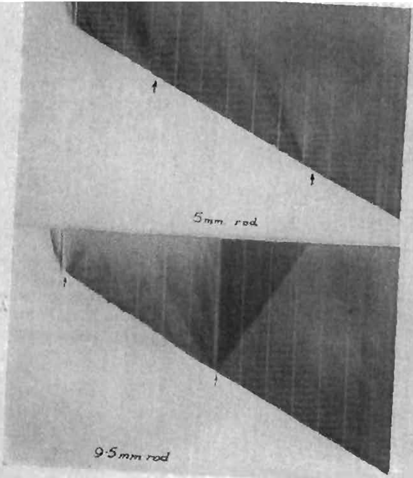
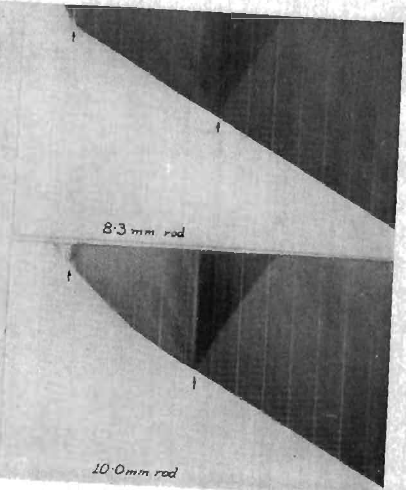


FIG. 13.



Vertical reference lines 10 cm. apart.

FIG. 14.

"top" and "front" windows was not satisfactory, because the aspects relative to the camera were not quite similar, one being normal and the other tangential to the tube. Moreover, through a window at the front of the tube, the flame would be visible both at the front and the back of the tube and the consequent doubling of the frequency of the striæ causes a loss of photographic resolution.

Both difficulties were overcome and two tangential views obtained by the use of a plate-glass mirror placed behind the tube and parallel to it. One image on the film record was made directly by the light from the flame as it passed a window near the top of the tube; the other image was produced by the light, after reflexion from the mirror, from the flame as it passed a window at the back. To prevent undesirable reflexions, the tube and the mirror were carefully screened, and in order that both images should be in focus, the aperture of the lens was considerably reduced. In spite of these precautions, a slight confusion on the film was caused by the unavoidable overlapping of the two images. Although this confusion was reduced by using a mixture (*e.g.*, $CH_4 + 6O_2$) which gave clear undulations on the trace of the flame front and very slight luminosity behind it, it was found that such mixtures often gave slightly irregular striations: for this reason carbon monoxide–oxygen mixtures were almost always used. The undulations were further apart and therefore easier to measure when wide tubes were used, but the size was limited by the fact that with tubes wider than 15 mm. the undulations and striæ were less regular.

Two negatives obtained when a 12·5 mm. tube, provided with windows 3·5 mm. wide, was used are reproduced in Fig. 2 (*a*) and (*b*). In each case the upper trace is the direct one, and the lower is that obtained by reflexion from the mirror. It is evident that the periodic character of the photograph is the same through whichever window the flame is seen. If a line is drawn parallel to the direction of motion of the film through each undulation, it is clear that in (*a*) each undulation in the direct image is distant $L/4$ (where L is the distance between successive undulations seen through one window) from the next on its left in the mirror image, whereas in (*b*) the phase difference is $3L/4$. The difference between the two records can be explained by assuming that in (*a*) the flame has passed round the tube in a clockwise direction, appearing first at the top window and then at the back window, whereas in (*b*) the direction has been counter-clockwise. The sense of the rotation is, in this case, apparently fortuitous and the same has been observed when other gaseous mixtures have been employed.

End-on Photographs.—Additional information regarding the rotary motion of the flame has been obtained by taking photographs

with the tube pointing directly towards the camera. Preliminary experiments had shown that the explosion tube could be placed within 80 cm. of the lens without the latter being damaged or displaced even though the tube itself was completely shattered. The explosion tube was clamped as rigidly as possible, and complete alinement between the axis of the tube and the axis of the lens was secured by the use of a spirit-level and by accurately placed sights similar to those used on a rifle. In order to reduce the amount of extraneous light that reached the camera, the explosion tube was made of copper instead of glass, and on the open end was placed a cap of black paper with an annular aperture (2 mm. wide), the outer edge of which coincided with the inner surface of the tube. With this arrangement, a disc of flame of uniform luminosity moving regularly towards the open end of the tube would produce, on the moving film, a continuous band; any periodic change of the luminosity of the flame—owing to periodicity, chemical or physical, in its propagation—would result in its being recorded as a series of rings. If, however, the foremost actinic portion of the combustion is small in size compared with the diameter of the tube and is rotating regularly about the axis of the latter, it should produce a record which is cycloidal in form. The type of cycloid produced would depend on the *apparent* peripheral rate of rotation of the flame, and this rate would be altered by changing the distance of the tube from the camera, other conditions remaining the same.

Figs. 3, 4, 5, and 6 are reproductions of some of the records obtained by the above method. They are clearly cycloids, and when compared with one another, show the alteration of type as the distance of the tube from the camera is altered. Since different parts of the terminal tube of the explosion gallery could not be at the same distance from the lens, there is a slight variation in type even in a single record, but as the length of the terminal tube was usually short compared with its distance from the camera, the variation is in most cases inappreciable.

The form of cycloids to be expected when the tube is at various positions in front of the camera can be calculated from the known velocity of the explosion-wave (V), the tube radius (r), and the distance L (see above). If the flame is travelling round the circumference of the tube, the arc traversed in time t will subtend an angle α at the centre such that $t = L\alpha/2\pi V$. It has been shown (J., 1927, 1575) that $L = 6r$ (approx.), and therefore $t = 3r\alpha/\pi V$. If the wheel had remained stationary during this period, the position of the flame image would be given by $x = \mu r \cos \alpha$; $y = \mu r \sin \alpha$, where μ is the magnification. But, since the film is moving vertically at a velocity W (the peripheral wheel velocity), each point on it has

moved forward, in time t, a distance $3r\alpha W/\pi V$. The trace of the flame image on the moving film is therefore the cycloid in which the above value of y is replaced by $y = \mu r \sin \alpha + 3r\alpha W/\pi V$. An example illustrates the method employed in plotting the theoretical cycloids :

Experiment 456. Mixture $CH_4 + 5\frac{1}{2}O_2$. Velocity of explosion taken as 1900 m./sec.; $r = 7{\cdot}5$ mm.; $\mu = 1/15$; $W = 53{\cdot}83$ m./sec. Hence the cycloid is $x = 0{\cdot}5 \cos \alpha$; $y = 0{\cdot}5 \sin \alpha + 0{\cdot}2030\alpha$. By taking different values for α, corresponding values for x and y were obtained. A curve was plotted from these values : it was then photographed and reduced in size for comparison with the record obtained in this experiment. Similar cycloids were plotted for each magnification and tube radius, and the reduced reproductions placed alongside the actual photographic records in Figs. 3—6. In each case, the value of μ taken is that which corresponds with the middle point of the horizontal part of the explosion tube : the theoretical and recorded cycloids, therefore, correspond most closely over the central portions of the latter.

The agreement between the theoretical and the observed results appears to point conclusively to a rotational movement of the flame. That the rotation may be in either direction seems clear from Figs. 5 (*a*) and (*b*), for in (*a*) the cycloid corresponds to a clockwise rotation, whilst in (*b*) it is in the opposite direction.

Helical Traces on the Walls of the Tube.—The " helix " theory is also supported by evidence of a nature quite different from that hitherto described. The inner surface of the terminal glass tube of a gallery of lead and glass sections was found, after several explosions, to be coated with a light deposit of lead dust in which was discernible a very incomplete network of markings apparently consisting of portions of clockwise and counter-clockwise helices. During attempts to repeat this observation and to obtain perfect records of this type, many different incombustible powders were tried as coatings for the interiors of the tubes. A light deposit of French chalk, which adhered fairly readily to the glass surface, was found to be most suitable. Two of the tubes so coated, and used each for one experiment only, have been photographed for us by Messrs. Flatters and Garnett of Manchester and are reproduced in Fig. 7. In both cases the mixture $2CO + O_2$ (containing $0{\cdot}7\%$ H_2) was used. The helical trace is, in each case, clearly marked; in Expt. 467 it is clockwise with respect to the forward movement of the flame, whilst in Expt. 468 it is counter-clockwise.

Both tubes were of 14·7 mm. bore and the average pitch of the helical trace, whose direct measurement is rendered easy by its uniformity and completeness, is very nearly 44 mm. This distance

may, with very small error, be considered identical with that between points in the tube corresponding to successive undulations in the photographic record of the foremost actinic portions of the flame associated with the explosion in a tube of the same diameter. It may be, indeed, that the dust trace shows the actual path traversed by this part of the flame but, on the other hand, it is conceivable that it is due to some invisible disturbance travelling ahead of the flame.

There are several other points of agreement between the photographic records and these helical dust traces. For example, the dust trace produced when the mixture $2CO + O_2$ (containing 1% H_2) was used showed greater regularity than that formed with the mixture $CH_4 + 6O_2$, just as the undulations obtained in the photographs of the flame in the carbon monoxide mixture were more regular than those in the methane mixture. Again, a slow (pre-detonation) flame in the same carbon monoxide mixture was found to give neither striæ in the photographs nor traces in the French chalk, and the well-established explosion-wave in electrolytic gas also gave negative results in both cases.

That the first luminous portion or "head" of the explosion traverses a helical path gives no explanation of the long striæ which are a striking feature of many of the photographs taken on a moving film. Such a luminous "head" to the combustion as it traversed a helical path in a tube provided with only a narrow window would be recorded on the film as a chain of well-marked points or short arcs, whilst the combustion behind the head, if uniformly distributed across the tube section, would produce a uniform background in the photograph. The record, therefore, although probably showing an undulated trace, would be devoid of striæ, and quite unlike any actually obtained.

The production of striæ can, however, be explained by making the further assumption that the most luminous portion of the gas behind the flame front forms a long slender "tail," which lies close to the wall of the tube and rotates with a frequency almost identical with that of the head. Such a rotation of the tail explains the observation that the frequency of the striæ photographed through a middle window is double that recorded through a top window, just as the frequency of the undulations in the photographic record produced by the head was doubled under similar conditions. Through a middle window, the tail is visible twice (at the front and the back of the tube) during each revolution, but with a top window, only once.

Photographs of the Flame in a Vertical Tube.—That this long tail is a reality, and that it rotates in the tube, is evident from the

following experiments. A vertical glass tube, 30 cm. long and of 28 mm. bore (2 mm. wall), was completely covered with black paper except for a 1 mm. horizontal slit round the semi-circumference on the optical axis of the camera lens. The lower end of the tube was rigidly joined, by a conical copper tube (expansion 15—28 mm. over a length of 63 cm.), to a 15 mm.-bore lead tube about 6 m. long. The whole gallery was filled with the mixture $2CO_2 + O_2$ (containing about 1% of H_2) and firing was effected, as usual, by a spark near the closed end of the lead tube. The photograph of the flame, as it passed up the tube, was taken on a film moving at 50 m./sec. Two typical records are shown in Figs. 8 and 9. It is clear that, although the tube was invariably shattered by the explosion, the most luminous part of the burning gases had passed the slit before this occurred.

If the head only of the flame had been rotating, the first recorded portion of the photograph would have been a well-defined point or short line followed by a general greyness of diminishing photographic intensity. The records, however, show a considerable number of well-defined lines of alternate positive and negative slope, and these are evidently produced by the passage of successive portions of a long slender tail first across the front and then across the back of the tube. The regularity of the zig-zag lines also suggests that the whole length of the highly luminous gas is moving round the tube at a velocity which is approximately constant.

The form of the tail. Since the head and the tail of the combustion are rotating in the tube with the same frequency, it seems probable that the tail is the still-luminous track of the head, a very intense local burning near the wall of the tube. The tail, therefore, may occupy the exact position of the path traversed by the head, or its position and form may be modified by the movement of the gases of which it is the most luminous part.

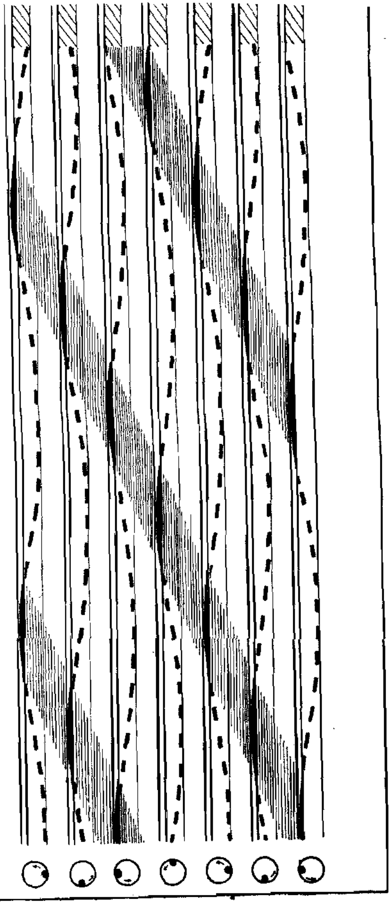
If, during an explosion, the gaseous mixture is, for the moment, assumed to remain at rest, and the head of the flame is traversing a helical path, the luminous tail would, at any instant, be helical in form—like a helical coil of wire lying in the tube. At a narrow horizontal window certain fixed points would be illuminated and should appear as *vertical* bars or *striæ* in the photographs. It is, however, almost certain that the gaseous mixture is being carried forward in the same direction as the explosion wave, for incandescent dust particles are, in many experiments, apparently carried forward at velocities approaching 1000 m./sec. If this be the case, the helical path of the tail should also be carried forward and produce striæ sloping in the *same* direction as the trace of the flame front. The records, however, show striæ which are never vertical but are either

horizontal or have a slight slope in the opposite direction, and it appears most improbable that a backward movement of the gases sufficiently rapid to produce striæ of this type and starting from the wave front, could take place. The hypothesis that the tail occupies the helical track of the head in gas which is at rest or moving parallel to the tube axis appears, therefore, to be untenable.

We are inclined to the view that, if the gaseous mixture were at *rest or moving only forwards or backwards in the tube, the track of* the head would be parallel to and probably near the wall of the tube, and that the tail would be a long narrow pencil of burning gas also parallel, or nearly parallel, to the axis of the tube. This would cause a uniform exposure of the photographic film. If now, *the gaseous mixture were set in rotation, the head and tail would* both appear intermittently at a horizontal window; the photographic trace of the head of the flame would be undulated, and each appearance of the tail would be recorded as a stria.

If the luminous pencil remained parallel to the axis of the tube whilst the whole mixture was rotating at constant velocity, it should produce horizontal striæ, and these have, in some cases, been observed. The striæ are, however, more frequently slightly inclined to the horizontal, and their slope may be accounted for in *one of two ways: either (a) the pencil of luminous combustion is* inclined to the tube axis, or (*b*) the rates of rotation of different parts of the burning gases are not identical.

Some information on this point may be obtained by comparing the vertical distance on the film between the ends of a single stria *with the width of a strip of film which would be affected by a* luminous inclined rectilinear tail as it passed once across a narrow window. Each point on a rectilinear tail must, in rotating, pass a window at the same angular velocity as the head of the flame: the *time of exposure t is therefore equal to $La/2\pi rV$, where a is the* length of arc visible through the window. Using a 3 mm. upper window in a 15 mm. tube, and neglecting the optical effects of the tube wall (which would still further restrict the field of vision), it is safe to assume that not more than one-quarter of the *internal circumference is visible. Hence $a/2\pi r < 0{\cdot}25$ and therefore* $t < 0{\cdot}25 \times 45/1750 \times 10^{-3}$, *i.e.*, $< 6{\cdot}4 \times 10^{-6}$ sec. During this time a film travelling at 50 m./sec. will be exposed over a vertical distance of $6{\cdot}4 \times 10^{-6} \times 5 \times 10^{4} = 0{\cdot}32$ mm. If, in addition, the tail should, at any moment, appear as a line inclined across the full width of the window, an additional strip of film, whose maximum width is that of the image of the window, will be exposed. In a typical experiment, where $\mu = 0{\cdot}06$ and the window is 3 mm. wide, the additional strip will be 0·18 mm. wide, and the total maximum width of film


Time axis

affected during the recording of each stria will be 0·32 + 0·18 = 0·50 mm. The vertical distance on the film between the ends of a single stria usually measures 1·2—1·5 mm., and it would therefore appear that, under the conditions of our experiments, a rectilinear tail of any possible slope cannot account for the production of striæ having both great length and appreciable inclination.

An alternative suggestion is that the pencil of luminous gas forming the tail is not rectilinear but is regularly distorted along its length so that it tends to assume the form of a helix. This distortion might be produced by a constantly diminishing speed of rotation of the gaseous medium as its distance from the head increased. Successive portions of this tail, therefore, would not appear at a horizontal window simultaneously but at successive time intervals, and would be recorded as sloping striæ (Fig. 10). The smallness of the slope suggests that the deviation of the tail from a straight-line form is slight, *i.e.*, that the helix is of great pitch. In those mixtures which do not allow of the formation of a long tail, the pitch of the tail helix may be so great that a complete turn may never occur. In other cases, the tail may be long enough for several turns of the helix to be luminous at the same time, and, through a narrow upper window, the corresponding points on each turn of the helix should be visible at any instant. The pitch of the helix, in these cases, may be estimated, therefore, by drawing a horizontal line—representing an instant of time—across one of the records so that it cuts two or more striæ; the length of the line thus intercepted is a measure of the pitch of the helix. Because of the lack of definition of the striæ, the measurement is only approximate, but in one case the pitch so estimated was found to be 46 cm., or about 10 times the pitch of the path of the head of the flame.

Insertion of a Coaxial Rod.—It was thought that some further information on the movements of the gases might result from experiments in which a glass rod was inserted into the tube coaxially with it, so as to offer to gaseous rotation an increased frictional resistance, while having a minimum effect upon any helical motion of flame in a still medium, if a propagation of this type took place.

The tube was 15 mm. in diameter, and the rods were 50—60 cm. long and 5—10 mm. thick. A rod was supported centrally by short, thin copper vanes attached at each end; these vanes offered only a slight resistance to the forward movement of the explosion. The mixture used was, in every case, $2CO + O_2$ (containing about 1% of H_2), and some of the records are reproduced in Figs. 11—14. When a 5 mm. rod was inserted, the forward velocity of the explosion-wave was quite unaffected, but, in the neighbourhood of the rod, the frequency of the striæ was appreciably decreased. Before and

beyond the rod, the undulations and the striæ had the normal frequency. When a rod of 8·3 *mm.* was used, its effect as an obstacle to the flame became evident, a strong pressure wave being reflected back through the burning gases from the end of the rod first encountered by the explosion wave: the striæ were not so well marked, and the flame velocity was not quite constant. A 9·5 mm. rod accentuated these effects, and the rod was shot from the tube, even though the end of the rod first encountered by the flame had been *tapered to a point. A 10 mm. rod appeared to offer an insur*mountable obstacle to the normal propagation of the flame. The pressure wave was very intense, and the rod was ejected from the tube: the flame velocity fell to about three-fifths of its former value, and the striæ were hardly visible.

TABLE I.

Effect of an Inserted Rod on the Pitch of the Undulations.
Diameter of Tube $(D) = 14·7$ *mm.*

Diameter of rod, mm.	—	5·0	8·3	9·5	10·0
Distance between undulations, *L*, mm.	44	53	55	61	indeterminate
L/D	2·99	3·61	3·73	4·16	—

The change in frequency of the striæ at the point where the rod was originally placed is not very abrupt; this may be due, in part at least, to the movement of the rod along the tube, for it was found difficult to make it very secure without using supports which were themselves obstacles to the explosion wave. The frequency of the striæ, however, becomes quite constant within a few centimetres, and is, in each experiment, much smaller in that part of the tube occupied by the glass rod than in the unobstructed portions of the tube. As the thickness of the rod is increased, the frequency of the striæ diminishes and the pitch (L) of the undulations undergoes a corresponding increase as shown in Table I. It appears reasonable to suppose that the narrower the annular space the greater will be the retarding effect of the viscous, frictional, or other forces on the speed of rotation of the gases, and the change in pitch of the undulations may indicate that such retardation has taken place.

Effect of Tube Form on the Rotation of the Gases.—It has been shown (J., 1927, 1575) that in uniform cylindrical tubes having diameters of 8—19 mm. the distance between successive undulations is approximately proportional to the tube diameter. This distance, which may be identified with the pitch of the helical path traversed by the head of the combustion, depends on the period of rotation of the gases and on the forward velocity of the flame. For any given mixture the latter is constant, and therefore the period of rotation

of the gases is proportional to the diameter, and hence to the circumference of the tube. That is to say, the *peripheral* velocity of rotation of the gases in the flame front is approximately constant in tubes of different diameters. This explains the gradual decrease in frequency of the undulations observed when a flame travels towards the wider end of a conical tube (Fig. 1).

The head, during each rotation in the wider part of the tube, traverses a longer path than the tail, which is still rotating in the narrower part: it will therefore appear at a horizontal window less frequently than points on the tail, and the end of the latter may become visible before the head passes across the window at a point nearer the wider end. Intermediate points on the tail will be similarly affected to a degree corresponding to the distance from the head, and the photographic records should show striæ sloping in the same direction as the trace of the flame front; such striæ are seen in Fig. 1.

The hypothesis of gaseous rotation may also explain the record (Fig. 7 of the previous paper; J., 1927, 1572) obtained when an explosion wave passes from a wide to a narrow tube. The velocity of the explosion wave remained unchanged, but the period of the undulations very rapidly became that characteristic of the narrow tube. The striæ in the two sections of the tube are not independent, as would be the case if the flame travelled along a helical path in a quiescent medium. If the gases are rotating at constant peripheral velocity in the two sections of the tube, as has been suggested above, the angular velocity of rotation will be greater in the narrow section. The change of velocity at the junction will, of necessity, be a gradnal one, and the period of rotation of the tail will therefore be unequal at various points along its length, decreasing towards the flame front. This would account for the great increase in backward slope of the striæ in the first few cm. of the narrow section of the tube.

Although the rotation of the medium would appear to account for the striæ, certain questions still remain unanswered. It is, for instance, not yet clear how such rotation is initiated, what conditions are necessary for its continued existence, and whether the absence of striæ when certain gaseous mixtnres are employed is due to the absence of rotation or to the predominant effect of other factors. Such prohlems as these are at present under investigation.

We should like to record our indebtedness to the Brunner Mond Research Fund, from which some of the apparatus has been purchased, and to the Department of Scientific and Industrial Research for a grant which has enabled one of us (A. C. F.) to devote his whole time to the work.

UNIVERSITY OF MANCHESTER. [*Received, April 11th*, 1928.]

CCLXXVI.—*Equilibrium Diagram of the System Antimony–Arsenic.*

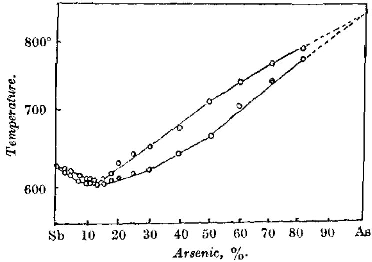
By Qasim Ali Mansuri.

The fact that commercial antimony contains small quantities of arsenic suggested the possibility of the formation of antimony–arsenic alloys, and as no such alloys have been described, the present investigation was undertaken.

Preparation of Materials.—Pure arsenic was prepared as described by the author (*J. Inst. Metals*, 1922, **28**, No. 2); and pure antimony was prepared from the pure trichloride by conversion into oxychloride, which was dissolved in concentrated hydrochloric acid, distilled, reprecipitated, and reduced with sodium carbonate and potassium cyanide.

Alloys.—Accurately weighed quantities of the two metals (40—50 g. together) were placed in hard-glass tubes which were evacuated, sealed, packed in sand in an iron tube, and heated in an electric furnace, thorough mixing being effected by a rocking movement applied to the furnace when the metals were sufficiently mobile.

Equilibrium diagram of the system antimony–arsenic.



Alloy No.	As, %.	Thermal arrests. 1.	2.	Alloy No.	As, %.	Thermal arrests. 1.	2.
1	—	632°	—	10	17·5	625°	613°
2	2·5	630	626°	11	20	637	615
3	5	626	620	12	25	650	624
4	7·5	622	612	13	30	662	630
5	10	616	608	14	40	690	654
6	11	614	607	15	50	716	680
7	12	612	607	16	60	746	710
8	13	605	—	17	70	772	745
9	15	615	607	18	80	792	778

Thermal Analysis.—The temperature of the cooling alloy was recorded by a suspended mirror galvanometer and scale connected with a thermocouple, the hot junction being applied in close contact with the outside of the alloy tubes by means of fireclay. The rate of cooling was about 8° per min. at high temperatures and about 5° per min. below 500°. A cooling curve was always repeated whenever there was any doubt as to its accuracy. Half-minute readings gave the foregoing thermal arrests, from which the equilibrium diagram of the system was constructed.

As none of the arsenic sublimed in the upper part of the glass tube or separated from the alloy, a chemical analysis of the alloys was considered unnecessary, and the composition was based on the weights of the two metals taken. The last alloy (80% As) was rather difficult to prepare, as the temperature required for its formation caused softening of the glass; and higher alloys could not be prepared for this reason.

The alloys freeze over a range of temperature and do not have a single sharp melting point. The first thermal arrest is the beginning of the freezing range and the second is the end.

Micrographic Analysis.—Suitable pieces of the alloy, polished as described previously (*loc. cit.*), were etched with ammonium sulphide and photographed, but owing to rapid oxidation of the surfaces the photographs are not suitable for reproduction. All the alloys proved to consist of a single constituent with a certain amount of coring; in the 80% arsenic alloy, fairly large six-sided crystals were observed.

Summary.

1. Arsenic and antimony alloy in all proportions.
2. They form solid solutions but no chemical compound.
3. The alloy containing 13% of arsenic freezes at the lowest temperature.

ALIGARH MUSLIM UNIVERSITY,
ALIGARH, INDIA. [*Received, February 27th, 1928.*]

CCLXXVII.—*Colloidal Platinum. Part IV. The Existence of Hexahydroxyplatinic Acid in Colloidal Platinum Solutions.*

By STUART W. PENNYCUICK.

IN Part III (this vol., p. 551) it was shown that solutions of colloidal platinum, when prepared by the Bredig method and with extreme precautions, contain a free strong acid which remains in solution

after the platinum has been coagulated. Those results are now confirmed, and evidence is produced that the strong acid is hexahydroxyplatinic acid.

Preparation and Procedure.—The colloidal platinum was made in water of specific conductivity (κ) less than 0·4 gemmho, and with the precautions previously outlined. Only relatively fresh sols were used, *i.e.*, those not more than a week old. After preparation, the sol was boiled for 20 minutes (unless otherwise stated) and then kept in the ice-box to minimise further changes. After 2 days the larger suspended particles appeared to have settled out, for the results outlined in this paper were not appreciably altered when the sols were centrifuged.

The titrations were carried out as described in Part II (J., 1927, 2600). The bases used were exactly $0{\cdot}001N$, and were kept in waxed bottles. A simple manipulation allowed of the transfer of the base to the titrating pipette and thence to the cell, without any contamination by atmospheric carbon dioxide.

Isolation of the Free Acid.—The evidence (Part III, *loc. cit.*) clearly indicated that the free acid was a strong acid, comparable in strength with hydrochloric acid. The titration curves (Part II) were, however, not strictly comparable with curves of strong acids, and the author concluded from such titrations that platinum sols were "really unique, and that they cannot strictly be compared either with strong or with weak acids." This apparent contradiction makes it fairly evident that the platinum particles themselves play a disturbing part during neutralisation of the platinic acid by the base.

Now, if the platinum sol is frozen into a solid block (from the outside to the centre), and then re-melted, the whole of the metal is completely precipitated. The solution remaining is not only as clear as water, but after standing or centrifuging, it shows no ultramicroscopic evidence of any remaining suspension. The conductivity of the clear solution is generally about 25% less than that of the original sol. This decrease is probably due to the smaller solubility of the free acid at the lower temperature. The original (and in fact a much higher) conductivity can be obtained by re-boiling the sample containing the coagulated platinum. The higher conductivities so obtained indicate that some of the platinic acid forms part of the colloidal particle. The coagulation by freezing is strictly irreversible.

Sols from which the platinum has been removed by freezing are designated throughout this paper as "coagulated (frozen) sols."

Titration of the Acid in the Coagulated (Frozen) Sol.—The acid being thus isolated, attempts were made to identify it; but owing

to the small quantity present (about 8 mg./l. in an ordinary sample), trustworthy quantitative methods were extremely difficult to apply. Titration of the coagulated (frozen) sol with various bases, however, would definitely test the previous evidence in favour of the acid being a strong acid. This would not only give some indication of the nature of the acid present, but a comparison of the titration curves with those obtained by the titration of the original platinum sol would afford some information as to the action between the added base and the colloidal particles.

Different samples of the coagulated (frozen) sol, of $\kappa = 10$—24 gemmhos, were accordingly titrated at 30° with calcium, barium, sodium, and potassium hydroxides. Since the first two bases gave

TABLE I.

[N = normality of added base, $\frac{1}{2}Ca(OH)_2$.]

Coagulated (frozen) sol–$Ca(OH)_2$.		Hexahydroxyplatinic acid–$Ca(OH)_2$.		H_2SO_4–$Ca(OH)_2$.	
$N \times 10^6$.	$\kappa_{30°}$.	$N \times 10^6$.	$\kappa_{30°}$.	$N \times 10^6$.	$\kappa_{30°}$.
—	15·55	—	15·68	—	15·73
15·0	11·48	9·7	12·77	13·1	11·88
23·6	9·20	17·8	10·34	24·2	8·69
32·0	7·40	24·8	8·40	30·2	7·08
38·8	7·27	29·4	7·26	34·7	6·43
45·6	8·29	36·0	6·83	43·2	7·57
53·8	9·90	40·4	7·46	50·9	9·16
61·5	11·71	48·0	9·06	60·0	11·48
71·3	14·06	55·5	10·85	67·4	13·46
78·6	15·89	62·8	12·74	71·6	14·53
87·2	18·05	71·2	14·87		

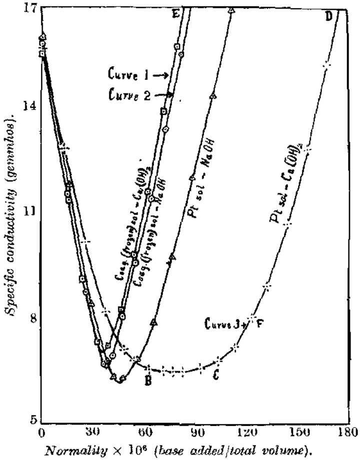
TABLE II.

(N = normality of added base.)

Coagulated (frozen) sol–NaOH.		Pt sol–NaOH.		Pt sol–$Ca(OH)_2$.	
$N \times 10^6$.	$\kappa_{30°}$.	$N \times 10^6$.	$\kappa_{30°}$.	$N \times 10^6$.	$\kappa_{30°}$.
—	15·96	—	16·15	—	15·82
15·1	11·64	16·0	11·91	12·7	12·94
25·5	8·79	29·5	8·47	25·2	10·28
35·7	6·70	38·1	6·81	37·1	8·22
40·5	7·00	41·2	6·37	47·5	7·14
47·4	8·10	46·8	6·34	53·0	6·83
55·6	9·66	55·3	6·87	62·1	6·57
63·6	11·51	65·2	7·93	70·6	6·53
72·8	13·54	76·5	9·82	76·1	6·53
81·6	15·68	88·5	12·12	81·6	6·54
		100·2	14·50	92·2	6·62
		111·8	16·98	102·7	6·83
				113·0	7·22
				122·9	8·07
				132·4	8·99
				143·9	10·77
				155·8	12·93
				167·5	15·39

similar results, only those for calcium hydroxide are shown; and for a like reason the results of the last two bases are illustrated by sodium hydroxide (see Tables I and II, and Fig. 1, Curves 1 and 2). The two curves are similar in shape and have almost the same minima, the sharpness of which is characteristic of titration curves of strong acids; moreover, weak acids give different types of curves with these two bases (see J., 1927, 2609). The sodium hydroxide curve shows the lower minimum, as would be expected from the

FIG. 1.



mobilities of the sodium and calcium ions, *viz.*, 58·3 and 69·96, respectively (see H. S. Taylor, "A Treatise on Physical Chemistry," 1924, p. 540). In each case the end-points agree satisfactorily with those calculated from the initial conductivities and ionic mobilities.

From this evidence one can conclude quite definitely that the free electrolyte present in platinum sols is a strong acid, and in view of the method of preparation it must be a platinic acid. Now only one such acid is known, *viz.*, hexahydroxyplatinic acid, $H_2Pt(OH)_6$, prepared and investigated by Wöhler (*Z. anorg. Chem.*, 1904, **40**, 423) and by Bellucci (*ibid.*, 1905, **44**, 168). These authors show that it

is a strong dibasic acid, more stable than the corresponding chloroplatinic acid, and that its salts undergo no hydrolysis at 25°. It therefore seemed probable that this was the acid formed during the preparation of platinum sols, but since it is described as being *insoluble*, an investigation of its solubility limits and its titration curve was necessary in order to strengthen this conclusion.

Preparation and Titration of Hexahydroxyplatinic Acid.—The acid was prepared by boiling chloroplatinic acid with excess of 10% sodium hydroxide solution, diluting the product, and neutralising it with acetic acid in the cold (see Bellucci, *loc. cit.*). The resulting white or yellowish-white precipitate was washed very thoroughly with conductivity water, being warmed with successive additions of 500 c.c. of the water for the final washings. The purified material, when heated to 60° with excess of conductivity water, gave an acid solution having $\kappa_{30^\circ} = 7{\cdot}5$ gemmhos, which increased to 36 gemmhos after 40 minutes' boiling in a borosilicate flask. Platinum sols when boiled for the same time in the same way showed a specific conductivity of about 25 gemmhos. (Various samples of conductivity water were subjected to the same treatment as controls, and always showed $\kappa < 0{\cdot}9$ gemmho.) It is thus evident that the solubility of the hexahydroxy-acid (on boiling) is quite sufficient to account for the conductivity of the platinum sols (also on boiling).

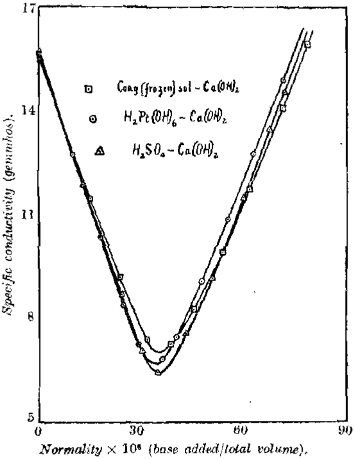
A complication now arises, however. Wöhler (*loc. cit.*) has shown that the white hexahydroxy-acid, which may be formulated as $PtO_2.4H_2O$, loses 1 mol. of water on boiling and gives an ochre-gold trihydrate, which is also probably a strong acid corresponding to $H_2PtO(OH)_4$. On prolonged boiling or on heating in the dry state, it is further dehydrated to the brown $PtO_2,2H_2O$ and then to the monohydrate, but the final molecule of water is very difficult to remove. These changes take place in the insoluble portion of the acid, but it is not known whether they also occur with the dissolved acid; it is certain, however, that the conductivity of the supernatant liquor is increased during these changes in the precipitate.

Owing to the above changes, the solubility product of the hexahydroxy-acid could not be determined. Also, the reason why the sample of hexahydroxy-acid was not boiled during the washing is now apparent.

If the ochre-gold product, or even the brown product, or a mixture of the two, be boiled with conductivity water, some passes very slowly into solution. Different samples of these solutions at widely varying stages of boiling were titrated with sodium and calcium hydroxides, and in every case the shape and position of the curves showed the solution to be that of a strong acid. Only one set of

results is given, *viz.*, that of the once-boiled hexahydroxy-acid * (boiled 25 minutes) when titrated with calcium hydroxide (see Table I and Fig. 2). This curve compares very closely with the corresponding curve for the coagulated (frozen) sol shown in the same figure. It is quite probable that a small and undetected amount of colloidal platinum remains in the coagulated (frozen) sol despite the freezing process. This platinum would cause a slight displacement in the titration curve which would account for the small divergence in the two curves.

FIG. 2.



In order to estimate the experimental error involved in the titration of these acid solutions of such low concentration, a very dilute sulphuric acid solution, stored and handled in exactly the same way as one of the previous solutions, was titrated with calcium hydroxide. The results are in Table I and Fig. 2. The normality

* Although this solution was considered to be the most comparable with the platinum sols (boiled 20 minutes), the boiled solutions of the lower hydrates (*e.g.*, $PtO_2,2H_2O$) showed titration curves whose turning points corresponded very closely indeed to that of the hexahydroxy-acid.

calculated from the initial specific conductivity is 0·000034, and that read from the curve is 0·000035. The conductivity at the turning point is calculated from the mobilities as 5·4 gemmhos, whereas the observed conductivity is 6·4 gemmhos: this difference may be attributed to the unavoidable contamination during boiling and handling.

Titration of the Platinum Sol.—Results for the titration of platinum sols have already been published (*J.*, *1927*, *2600*), but they were repeated on material prepared in such a way that the curves should be strictly comparable with those obtained from the coagulated (frozen) sols. A sample (800 c.c.) of the pure sol was prepared in the usual manner and divided into halves; one half was frozen, and the subsequent solution formed the coagulated (frozen) sol, whilst the other half was titrated directly with sodium and calcium hydroxides (see Table II and Fig. 1). Comparison of these curves with those for the free electrolyte itself (Curves 1 and 2) shows the part played by the platinum particles when the sol is titrated.

Discussion.

The foregoing experiments afford strong evidence that the free acid present in platinum sols is the strong hexahydroxyplatinic acid, probably in conjunction with some of its lower hydrates. Further, the conclusion that some of the platinic acid forms part of the colloidal particle is strengthened by the following direct evidence. If the sol be siphoned over from the dregs soon after preparation, and then centrifuged, the conductivity on boiling increases markedly —from approximately 6 to 25 gemmhos, or even higher. As has been shown, the whole of this conductivity can be ascribed to the strong acids present, and these must have separated from the colloid particle during boiling. It might be suggested that the acid is really formed during boiling by the oxidation of the finely divided particles, but this is not so, for on continued boiling (without loss of volume) a maximum conductivity of approximately 39 gemmhos is reached after about 8 hours—further boiling gives no further increase but ultimately causes coagulation. Also, if the preparation and the boiling take place in an atmosphere of nitrogen, exactly the same results are obtained. We must conclude, then, that the boiling actually liberates the acid from the colloid particle. Further, if a sol with a specific conductivity of 17 gemmhos is centrifuged, coagulated by freezing, and then boiled for 2 hours, the conductivity increases to about 28 gemmhos, thus leading to the same conclusion. Incidentally, it may be mentioned that if the dregs from the original preparation be washed in the cold, and then boiled with conductivity water, the very small conductivities obtained, about

5 gemmhos, indicate that very little acid is carried down by the dregs.

From the total evidence produced, the author interprets the formation of the colloid particles in the following way. During the sparking process and the atomisation of the platinum, some oxidation occurs, probably at one of the poles, with the formation of molecules of hexahydroxyplatinic acid. The anions of the strong acid condense with platinum atoms to build up aggregates of $Pt-H_2Pt(OH)_6$. Each particle thus acts as a multivalent acid micelle of perhaps very high valency. The acid molecules, or at least those at the surface of the particles, tend to ionise. The ionisation of such a multivalent micelle is still open to investigation, but we can well imagine that such ionisation would be relatively slight owing to the big residual charge that would result. As, however, the bound acid is a strong acid, the tendency to ionise will be particularly great, and the result may be interpreted as a dynamic equilibrium at the surface which gives rise to the so-called double layer.

We are now in a position to discuss the titration curves shown in Fig. 1. The wide divergence between the Pt sol–$Ca(OH)_2$ curve and the corresponding coagulated (frozen) sol–$Ca(OH)_2$ curve is very striking, and indicates that the colloidal platinum particles remove considerable quantities of calcium hydroxide. In the absence of evidence to the contrary, the most satisfactory explanation of the removal of the base appears to be the simplest chemical explanation, *viz.*, that on the gradual addition of calcium hydroxide to the platinum sol, the greater part of the base is neutralised by the free platinic acid, but a small amount is neutralised by the acid at the surface of the colloid particle. This proceeds until the whole of the free acid is neutralised, up to, say, the point B on Curve 3. Any further base is then completely neutralised at the surface of the particles to form the calcium salt of the hexahydroxyplatinic acid which is bound at the surface. The early coagulation of the platinum after the point C indicates that the tendency of the micelle to ionise is not very great, *i.e.*, that the double layer at the surface is disappearing.

At the points E and D, we have the same quantity of calcium hexahydroxyplatinate present—assuming that none has diffused away from the colloid surface in the case of the point D. Further, since the conductivities at these two points are the same, and calcium hydroxide is the only other electrolyte present, it follows that the difference in concentration at E and D represents the amount of base removed by the colloid particles. This difference is $0{\cdot}000091N$, and the surface acid neutralised by this excess of base would also be represented by $0{\cdot}000091N$, which in the free state would give rise

to a conductivity of 39 gemmhos. When the sol was boiled till it gave a maximum conductivity, the total increase found, due to the liberation of the bound acid, was only 23 gemmhos. The difference of 16 gemmhos may be due to the boiling process not liberating the whole of the acid, or perhaps to the solubility limit of the hexa-hydroxy-acid, the highest conductivity found for the boiled hexa-hydroxy-acid being of the order 36 gemmhos.

The Pt sol–NaOH curve (Fig. 1) is essentially different. The relative sharpness of the turning point and the high coagulation concentration indicate that the double layer is more difficult to destroy, and that therefore the sodium salt at the surface of the micelle ionises more freely. Speaking generally, we may say that the greater coagulating power of bivalent bases is due to the formation on the micelle of surface salts, which when so held show a smaller tendency to ionise. This is in keeping with the well-known fact that bivalent bases are less ionised than univalent bases at comparable concentrations.

Two further circumstances may be emphasised. (1) The platinum sol was generally prepared in a stream of carbon dioxide-free air, but this atmospheric oxygen was not responsible for the oxidation of the platinum to the hexahydroxy-acid during sparking, for a preparation carried out in a stream of nitrogen gave strictly comparable conductivities, and on boiling and titration (in a stream of nitrogen) the same set of curves was obtained. (2) If the freezing mixture used during the preparation be dispensed with, and the sol be allowed to become warm, there is always more platinum wastage and a much weaker sol results. This cannot be ascribed to coagulation by heat, for platinum sols can be boiled quite safely for several hours. Now it has been shown that hexahydroxy-platinic acid must be prepared in the cold, and it would therefore appear that the initial preservation of the acid (by the use of a freezing mixture) is essential to the preparation of a strong stable sol.

Summary.

The existence of a strong (free) acid in colloidal platinum sols has been verified by coagulating the platinum by freezing and then titrating the remaining clear solution.

It is believed that there is present either the strong hexahydroxy-platinic acid or a mixture of this acid with some of its dehydrated forms.

Evidence is produced that the hexahydroxy-acid enters into the structure of the colloid particle, and it is suggested that ionisation of the surface acid accounts for the stability of the colloid.

Coagulation of platinum sols by bases is discussed in terms of the neutralisation of this surface acid.

The author is very much indebted to Mr. A. E. Scott, B.Sc., for the preparation of the sample of hexahydroxy-acid used in this work.

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CCLXXVIII.—*The Pectin and Hemicelluloses of the Flax Plant.*

By STANLEY THOMAS HENDERSON.

ON the constitutive problem of the plant pectins the most important papers are those of von Fellenberg (*Biochem. Z.*, 1918, **85**, 118), Ehrlich (*ibid.*, 1926, **168**, 263; **169**, 13), and Nanji, Paton, and Ling (*J. Soc. Chem. Ind.*, 1925, **44**, 253T). Von Fellenberg and Ehrlich extracted their material from plants by water boiling under pressure, whereby products were obtained differing considerably from the "ammonium oxalate pectin" described in the present work.

1. *The Ammonium Oxalate Pectin.*—Flax fibre separated mechanically from the unretted straw was extracted with hot dilute (0·5%) ammonium oxalate solution, and the pectin worked up in the usual way, the characteristic methoxyl groups being removed by alkaline hydrolysis. There remained a substance which from analysis and properties was galactosetetragalacturonic acid, $(C_6H_{10}O_5,4C_6H_8O_6 - H_2O)_n$. This has roughly the same ultimate composition as the hypothetical galacto-arabino-tetra-galacturonic acid, $C_{35}H_{50}O_{33}$, considered by Nanji, Paton, and Ling to represent the demethylated form of the pectin complex. But the calculated amounts of carbon dioxide liberated from the "-uronic anhydride" groups by boiling hydrochloric acid (*d* 1·06) are, respectively, 20·7 and 17·6% for these two molecules. Some of Nanji, Paton, and Ling's estimations did, in fact, approach the higher figure, and in the present work it was observed that the yield of carbon dioxide rose steadily to 20·9% with repeated purification of the pectin. Nanji, Paton, and Ling evidently did not complete the separation of the pectin gel from adsorbed carbohydrate produced, presumably, by hydrolysis of the original pectin complex.

It appeared impossible by precipitation methods to render the pectin free from inorganic matter and a small residual methoxyl content. A copper salt was prepared in an attempt to obtain a

more nearly homogeneous product. Determinations of "-uronic anhydride" on the copper salt were, however, very variable, but the quantities of carbon dioxide evolved in the reaction were large enough to rule out the possibility of any non-carboxylated residue in the molecule. This therefore appeared to be

$$3(C_6H_7O_6)_2Cu,2C_6H_8O_6,4H_2O.$$

Hydrolysis of the ammonium oxalate pectin with boiling dilute sulphuric acid gave an almost insoluble polygalacturonic acid, $(C_6H_8O_6)_n$ or $(4C_6H_8O_6,H_2O)_n$. From this reaction were also obtained a small amount of a soluble acid, giving a soluble barium salt, and a syrup containing arabinose, galactose, and a little fermentable hexose of unknown origin. The arabinose in the syrup might arise from adsorbed pentose (see above), or from partial decarboxylation of galacturonic residues.

A better yield of the polygalacturonic acid resulted from hydrolysis with 1% hydrochloric acid. A highly purified specimen (A7) agreed with the formula $(C_6H_8O_6)_n$. Besides this main substance the same barium salt was obtained as in the sulphuric acid hydrolysis.

Ehrlich described two "digalacturonic acids" derived by hydrolysis of the "pectic acid" of sugar beet, namely, insoluble $2C_6H_8O_6,H_2O$ (*a*) and soluble $2C_6H_8O_6$ (*b*). From his flax "pectic acid," only the soluble *b*-acid could be produced. In the present work the main yield closely resembled his *a*-acid in properties. Differences in molecular weight or configuration may be involved. Exception may reasonably be taken to some of Ehrlich's results, for in determining the equivalent of "digalacturonic acid *b*" from flax pectin he recorded titrations differing from the calculated value by 22, 26, and 31% for three separate preparations, although the ash content of the material, to which these discrepancies were attributed, was less than 1% in the single instance where it was determined.*

For simplicity it has been assumed in the above discussion that the carboxylated groups in pectin and its hydrolysis product are entirely galacturonic acid and not glycuronic residues. This has been indirectly demonstrated by the workers already mentioned, although direct quantitative proof is lacking.

2. *Hemicellulose extracted by Water under Pressure.*—When flax fibre or straw, after a preliminary leaching with hot water, was subjected to the action of water under pressure at temperatures between 100° and 145°, various soluble substances were extracted

* In a recent descriptive paper (*Z. angew. Chem.*, 1927, **40**, 1305) Ehrlich has discarded these "digalacturonic acids" in favour of his earlier views on "tetragalacturonic acids."

in the form of calcium-magnesium salts. This was Ehrlich's method of preparing " calcium magnesium pectate " from whole flax straw, but the chemical and genetic relations between the non-gelatinous, easily soluble " pectic acid " so derived and the ammonium oxalate pectin are obscure. It appears desirable, if only for convenience of description, to restrict the term " pectin " to gel-forming substances of high carboxyl content such as the " ammonium oxalate pectin."

Even when purified from adherent tissues, waxes, pectin, and free hemicelluloses, flax fibre still contained carboxylated hemicellulose (CO_2, 5·2%) soluble in water under pressure (Cashmore, J., 1927, 718). The distinction between pectin and non-pectic hemicellulose was evident in this case. The salts and acids resulting from pressure extraction will therefore be referred to as carboxylated hemicellulose, or non-pectic hemicellulose.

On the question of the possible derivation of non-pectic hemicellulose by degradation of pectin, no definite evidence can be given, except that the autoclave treatment for removal of hemicellulose left behind no pectin soluble in ammonium oxalate. On the other hand, purified ammonium oxalate pectin heated with water under similar conditions was converted into a syrup with no recognisable constituents except -uronic residues.

In the present work, two preparations of hemicellulose were made from unretted flax fibre, and one from unretted flax straw. The first two agreed fairly well with the empirical formula $C_6H_{10}O_5$, and yielded 5·6 and 4·3%, respectively, of " -uronic " CO_2.

The extract from whole straw was first purified and analysed as a calcium magnesium salt with 9·7% of -uronic carbon dioxide. Conversion into the free acid lowered this value to 6·04%. Once again, however, the acid corresponded to the formula $C_6H_{10}O_5$. Part of the material obtained by repeated extraction of the straw at higher temperatures gave only 2·74% of carbon dioxide. Ehrlich's so-called " pectic acid " from flax had a higher oxygen content and 13·0 and 13·9% of -uronic carbon dioxide. These varied figures suggest that mixtures of hemicelluloses were produced by pressure extraction. The calcium magnesium salt from straw was a soluble, amorphous powder agreeing closely with the formula $(C_6H_7O_6)_4CaMg,(C_6H_{10}O_5)_6,H_2O$.

3. *Hexopentosan from Flax Straw.*—The yield of calcium magnesium salt was less than 2% on the weight of straw. A more abundant product (5%) was a solid hexopentosan free from -uronic residues. Pentose estimations indicated the presence of equivalent amounts of hexosan and pentosan, and hydrolysis gave galactose, arabinose, and xylose, also a small amount of fermentable hexose.

Note on the Estimation of Pectin.

Since hemicelluloses without the gel-forming characteristics of pectin may contain -uronic groups, it is clearly inadmissible to estimate pectin in flax straw or fibre, or in other tissues containing cellulose, by determining the carbon dioxide evolved on boiling with hydrochloric acid (*d* 1·06). For example, ripe unretted flax fibre separated mechanically from the straw contained 7·0 to 7·8% of -uronic anhydride in several samples, whereas the pectin found by the precipitation method (*Biochem. J.*, 1922, **16**, 60) was only 4·5 to 5%. This fibre, when all adherent tissues had been removed by repeated treatment with hot soap solution, still contained 1·6% of -uronic anhydride in the cleanest sample examined. After ammonium oxalate extraction this value fell to 1·3% (compare Cashmore, *loc. cit.*). A further source of error is the carbon dioxide derived from oxycelluloses under the conditions of estimation.

In Carré's method of estimation (*Ann. Bot.*, 1925, **39**, 811) the pectin is extracted by boiling *M*/75-hydrochloric acid, and precipitated as a calcium salt. This process applied to clean flax fibre lowered the -uronic anhydride content from 1·9% to 0·3%, but the calcium salt amounted to 0·03% only. Further extraction with boiling *M*/100-sodium hydroxide to remove "middle lamella pectic substance" left the -uronic anhydride content unchanged at 0·3%.

EXPERIMENTAL.

1. *Ammonium Oxalate Pectin.*—The straw used was "J. W. S." flax pulled when ripe; the fibre was removed by breaking, scutching, and hackling without retting. Tannins and other soluble substances were removed by one or two extractions with water at 80—90° for a few hours.

One extraction lasting about 7 hours with ammonium oxalate solution (0·5%) at 80—90° was sufficient to remove most of the pectin. 100 G. of fibre, or tow from the hackling, required about 1 l. of liquid. After extraction the filtered liquid was precipitated by an excess of alcohol to give a pale yellow gel. The solid was finally squeezed nearly "dry" in a linen cloth, redissolved in water to not more than 0·5% concentration, reprecipitated by alcohol with a little hydrochloric acid, and so on. Hydrolysis of methoxyl groups was effected by making the aqueous solution of pectin alkaline (*N*/40 in NaOH) and leaving it for about 18 hours at room temperature before adding acid and alcohol. Finally, the gel was macerated with 90% alcohol, then with alcohol and ether, and dried to constant weight in a vacuum over phosphoric oxide. The dried product was pale cream in colour, granular and hard to powder,

and very slowly soluble in cold water. Excess of acid precipitated it from aqueous solutions, and salts of the alkaline earths at once produced colourless gels. Tollens's naphtharesorcinol reagent gave a violet ethereal extract indicating the presence of galacturonic (or glycuronic) groups. Oxidation with nitric acid (*d* 1·15) on the water-bath gave a small yield of mucic acid presumably derived from the galactose residue, for experiments on polygalacturonic acid failed to produce mucic acid except by the slow action of concentrated nitric acid.

Two samples were analysed: (*a*) six times precipitated, and twice hydrolysed in *N*/40-sodium hydroxide: ash, 1·5%; (*b*) ten times precipitated, and five times hydrolysed in *N*/40-sodium hydroxide: ash, 0·9%. Found, on ash-free basis: (*a*) C, 41·8, 42·2, 41·8; H, 5·0, 4·6, 5·0; CO_2 from -uronic anhydride, 19·7, 20·3, 19·7. (*b*) C, 41·4; H, 5·1; CO_2, 20·9; OMe, 0·77; equiv. by back titration with phenolphthalein as indicator, 228·6. $C_6H_{10}O_5,(C_6H_8O_6)_4 - H_2O = C_{30}H_{40}O_{28}$ requires C, 42·4; H, 4·8; CO_2, 20·7%; equiv., 212·1; one methoxyl group per molecule requires OMe, 3·6%. $C_{30}H_{42}O_{29}$ requires C, 41·6; H, 4·9; CO_2, 20·3%; equiv., 216·6. A thrice precipitated sample, not hydrolysed, gave OMe, 2·2; CO_2, 19·3%.

2. *Copper Salt.*—Pectin purified by several precipitations and hydrolyses was dissolved in water at 70—80° to give a solution of about 0·3% concentration, to which was added one-tenth of its volume of *N*-acetic acid, followed by twice this amount of *M*-copper sulphate solution. The mixture was stirred and heated at 80° for an hour, and the gelatinous copper salt was separated, washed free from soluble copper compounds with large quantities of very dilute, hot acetic acid and then with hot water, alcohol, and ether in succession, and dried to constant weight in a vacuum over phosphoric oxide. It formed hard, granular masses of a bright green colour. Not more than about 4 g. could be conveniently prepared in one operation [Found: C, 34·3; H, 4·2; Cu, 11·3 (mean of seven combustions on three different preparations). $(C_6H_7O_6)_8H_2Cu_3,4H_2O$ requires C, 34·6; H, 4·0; Cu, 11·45; CO_2, 21·1%.

$$C_6H_{10}O_5,(C_6H_7O_6)_4Cu_2,3H_2O$$

or $C_{30}H_{36}O_{28}Cu_2,4H_2O$ requires C, 34·5; H, 4·25; Cu, 12·2; CO_2, 16·9%].

The -uronic anhydride estimation gave values for CO_2 varying from 18·0 to 19·8%, and concordant results could not be obtained for any single sample. Taking the elementary analyses and the *maximum* value found for CO_2, it is possible to deduce the formula $C_{32}H_{46}O_{35}Cu_2$, containing *five* -uronic groups. The number of carbon atoms could hardly be explained by the presence of methoxyl

on boiling, was stained brown by iodine, and gave a positive naphtha-resorcinol reaction (Found, on ash-free basis : C, 44·8, 44·6 ; H, 6·3, 6·1 ; " -uronic " CO_2, 5·57 ; ash, 4·0. $C_6H_{10}O_5$ requires C, 44·4 ; H, 6·2%).

Another preparation was finally precipitated from water by *strongly acid (HCl) alcohol.* The ash content fell to 0·6% (Found : C, 45·0 ; H, 6·3 ; " -uronic " CO_2, 4·32 ; *OMe*, 1·24 ; *equiv.*, corrected for methoxyl, 1290).

(2) 450 G. of broken, unscutched straw were used in an experiment similar to Ehrlich's. Soluble substances were removed by extraction with water at 50°. There followed five extractions for hemicellulose, first for 2 hours in 5 l. of water at 30—35 lb. per sq. in. excess pressure, then similarly at higher pressures up to 50 lb. per sq. in. From the straw, now considerably darkened, no pectin could be extracted by ammonium oxalate, although cold *N*-caustic soda removed " free hemicelluloses " precipitable by excess of acetic acid.

The aqueous extracts were concentrated to small bulk on the water-bath, and the yellow, flocculent " calcium magnesium pectate " precipitated by alcohol. That from the first pressure extract (P_1) was worked up separately from the less pure material (P_2) arising from later extracts. The aqueous-alcoholic filtrates from P_1 and P_2 were evaporated under reduced pressure, and fractional precipitation then separated a gummy substance, soluble in water but insoluble in alcohol, from the main yield, which was soluble in both solvents. The aqueous-alcoholic solution of the latter was concentrated and freed from a resinous substance soluble in alcohol but insoluble in water. The hexopentosan present in the aqueous solution was finally obtained as a brown, brittle solid (23 g.) by concentration to a syrup and drying in a vacuum over sulphuric acid.

Calcium magnesium salt from whole straw. This, after treatment with norit and precipitation by alcohol, formed a pale yellow or brown powder easily soluble in water or dilute acid. That described above as P_1 (yield, 4·5 g.) gave, after four precipitations, C, 41·1, 41·1 ; H, 5·4, 5·0 ; CO_2, 9·7 ; ash (CaO, MgO), 5·46, 6·13%. The weights of ash, assumed to be CaO and MgO in equivalent quantities, gave (Ca + Mg), 3·64, 4·08%. $(C_6H_7O_6)_4(Ca + Mg),6C_6H_{10}O_5,H_2O$ requires C, 41·0 ; H, 5·2 ; CO_2, 10·0 ; (Ca + Mg), 3·67%.

The fraction P_2 (yield, 3·7 g.) was converted into the soluble acid by three precipitations from dilute hydrochloric acid (Found : CO_2, 2·74%). The main yield P_1 was similarly treated (Found : C, 44·4 ; H, 6·4 ; CO_2, 6·04. $C_6H_{10}O_5$ requires C, 44·4 ; H, 6·2%).

Hexopentosan. Oxidation with nitric acid (*d* 1·15) yielded mucic acid, denoting the presence of galactose residues. Bial's orcinol reaction for pentoses gave a positive result, but the tests for methyl pentose and -uronic groups failed (Found, by the Krüger–Tollens–Kröber method: pentosan, calc. as a mixture of arabinose and xylose, from Kröber's tables, 44·0, 40·9. $C_5H_8O_4,C_6H_{10}O_5$ requires pentosan, 44·9%).

The dried solid (5 g.) was hydrolysed by boiling for 4 hours with 250 c.c. of 1% sulphuric acid. Excess of barium carbonate and charcoal were added to the hot liquid, which was filtered, concentrated to a dark brown syrup under reduced pressure, and dried in a vacuum over sulphuric acid. Arabinose was identified in it by the diphenylhydrazone, xylose with difficulty by Bertrand's reaction. Oxidation with nitric acid gave mucic acid as for the unhydrolysed substance. No methyl pentose, ketose, or -uronic groups were distinguished. By the method previously outlined, it was determined that the syrup contained 4·5% of yeast-fermentable hexose calculated on the total reducing sugars.

The author's thanks are due to the Linen Industry Research Association for permission to publish these results; also to Mr. C. R. Nodder and Dr. A. E. Cashmore for helpful advice and criticism.

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CCLXXIX.—*Resolution of Racemic Chlorobromoacetic Acid.*

By Hilmar Johannes Backer and Hindrik Willem Mook.

The remarkable behaviour of chlorobromomethanesulphonic acid, which according to Read and McMath (J., 1925, **127**, 1572) does not show optical activity in aqueous solution, led us to examine the related carboxylic acid, chlorobromoacetic acid, $CHClBr{\cdot}CO_2H$.

A preliminary study * had already shown the possibility of resolution. In the meantime Read and McMath stated (J., 1926, 2183) that only in some organic solvents might salts of optically active chlorobromoacetic acid be obtained, and in water, in consequence of immediate racemisation, no activity could be observed. A renewed investigation by the same authors (J., 1927, 537) failed to confirm our results.

We have now completed the resolution of this acid, have measured the molecular rotations of acid and salts, and have calculated the

* Communicated to the British Association (Oxford, August 1926) and to the Academy in Amsterdam (June 1926).

(0·198N). showed $\alpha_D = + 0{\cdot}21°$ ($l = 2$). The rotation of the sodium salt was thus $[M]_D = + 6{\cdot}3°$.

The rotatory power of the free acid in aqueous solution is greater than that of the sodium salt and of opposite sign; it depends on the concentration and is raised by addition of strong acids. The reason is that chlorobromoacetic acid is a fairly strong acid which dissociates to a considerable extent in solution, giving an anion of opposite rotation.

The rotation of the undissociated acid cannot be measured by addition of sulphuric acid in excess, because the dissociation is not sufficiently reduced. Therefore the rotation of the pure acid was measured in different concentrations at 17°, and also the degree of dissociation was calculated from the dissociation constant by means of the equation $K = \alpha^2c/(1 - \alpha)$. The value of $K_{17°}$ was found to be $8{\cdot}1 \times 10^{-2}$.

The active acid was prepared by decomposing the brucine salt with sulphuric acid, extracting the chlorobromoacetic acid with ether, drying the solution with fused sodium sulphate, and evaporating the ether in a current of dry air at the ordinary temperature. The pure active acid was dissolved in water, and its concentration determined by titration.

If the molecular rotation observed for the mixture acid–ion is represented by M_m, the unknown rotation of the acid by M_a, and the rotation of the ion by M_i (= 6·3°), we have $M_m = \alpha M_i + (1 - \alpha)M_a$ or $M_a = (M_m - 6{\cdot}3\alpha)/(1 - \alpha)$.

c (g.-mol./l.).	$\alpha_D$obs. (l=2).	M_m.	α.	M_a.
0·150	−0·335°	−11·2°	0·50	−28·6°
0·208	−0·525	−12·6	0·44	−27·5
0·250	−0·695	−13·9	0·42	−29·0
0·347	−1·14	−16·4	0·37	−26·0

The average value of $[M]_D$ for the undissociated acid is − 28°.

The rotations of the salt and of the acid were measured for different wave-lengths in order to determine the rotatory dispersion :

λ ($\mu\mu$)................................	656	589	546	516	486
Anion (sodium salt) : [M] ...	+4·8°	+6·3°	+7·4°	+8·3°	+9·1°
Undissociated acid : [M] ...	−22°	−28°	−36°	−42°	−50°

Racemisation of Active Chlorobromoacetic Acid.—An aqueous solution of the free acid does not show any tendency to racemise at the ordinary temperature. The salts racemise, but very slowly.

Only in presence of an excess of a strong base is the velocity of racemisation appreciable. Under these conditions, accurate measurements of the velocity coefficient are difficult, because the acid hydrolyses when it is kept for a long time in alkaline solution;

hydrogen halide is formed and the quantity of free alkali diminishes. The experiments were therefore stopped when the solutions gave a turbidity with nitric acid and silver nitrate. The velocity coefficient was calculated by aid of the formula $k = (\log \alpha_1 - \log \alpha_2)/t$. For a larger number of observations (*e.g.*, 4), Schmid's method (*Z. physikal. Chem.*, 1926, **119**, 8) was used,

$$k = (\log \alpha_1 + \log \alpha_2 - \log \alpha_3 - \log \alpha_4)/(t_3 + t_4 - t_1 - t_2).$$

Time was expressed in hours and Briggsian logarithms were used. The rotations were measured for the D and E lines in a tube of 2 dm. and their sum, $\alpha_D + \alpha_E$, was substituted for α in the formula.

1. *Acid solution.* Chlorobromoacetic acid (0·08 g.-mol./l.) in presence of sulphuric acid (1·38 equivs.) at 25°. The rotation, 0·65°, did not change in 77 hours and therefore there was no racemisation.

2. *Acid solution.* The same acid solution as in experiment 1 was examined at 100°. Titration of the acid, 1·46 equivs. per litre. The rotation was 0·665° and fell in $3\frac{3}{4}$ hours to 0·445°. The concentration of the acid titrated had not changed. Racemisation constant $k_{100°} = 4·5 \times 10^{-2}$. After $16\frac{3}{4}$ hours the solution was red and the quantity of acid had increased to 1·54.

3. *Neutral solution.* A solution of the ammonium salt with the rotation − 0·14° was kept at the ordinary temperature. After 90 days the rotation was −0·11° and after 570 days −0·07°. The racemisation of the salts in neutral solution is therefore negligible.

4. *Chloroform solution of a salt.* The racemisation of the brucine salt was studied in chloroform solution, because according to Read and McMath (J., 1926, 2184) salts of active chlorobromoacetic acid are stable in this solvent. A solution of 2 g. of the brucine salt in 25 c.c. of chloroform and 5 c.c. of methyl alcohol was examined at 25°; the lævorotation increased gradually owing to racemisation of the dextrorotating component.

t (hours)	0	96	321	417	489	652
$\alpha_D + \alpha_E$	−1·04°	−1·09°	−1·29°	−1·42°	−1·55°	−1·68°

This racemisation, therefore, is not slower, but much faster than the racemisation of the neutral salts in water.

5. *Alkaline solution.* 0·15 G.-mol. of sodium chlorobromoacetate and 0·049 g.-mol. of sodium hydroxide per litre. Temperature 25°. The rotation observed was 0·325° * and after 4 hours 0·145°. The final titration indicated the presence of 0·047 g.-mol. of base, so that the hydrolysis was negligible. Racemisation constant $k_{25°} = 9 \times 10^{-2}$.

* For the pure active salt this value ($\alpha_D + \alpha_E$) should be 0·43°. The salt was thus one quarter racemic, which does not affect the calculation of the velocity coefficient.

formed in this case. The main product of the reaction is a substance, *α-di-p-toluenesulphonyl-2-phenylnaphthylene-1 : 3-diamine*, which is soluble in alkali and, like the α-dimethyldiamine, is dimorphic, the two forms having m. p. 188—189° and 203—205°, respectively. The lower-melting form, which has been designated α_1-, is obtained when the sulphonamide is precipitated from alkaline solution by acidification or when it is recrystallised from ethyl alcohol in such strength that crystallisation does not take place until the ordinary temperature is reached. When the lower-melting form is melted in a capillary tube and allowed to resolidify, it undergoes conversion into the higher-melting form. The α-, or stable, form of the disulphonamide separates when crystallisation takes place from a hot solution. Both forms crystallise in prisms and the dimorphic relationship was confirmed by Sidgwick's method (J., 1915, **107**, 672).

The alcoholic mother-liquor from which the α-disulphonamide had been removed contained a second disulphonamide, which, after repeated crystallisation from methyl alcohol, was obtained in soft needles, m. p. 173—175°. This substance was only obtained in sufficient quantity for analysis, bnt in all probability it is β-*di*-p-*toluenesulphonyl-2-phenylnaphthylene*-1 : 3-*diamine* corresponding to the β-form of the dimethyl base.

In addition to the α- and β-disulphonamides, which are soluble in alkali, two other suhstances were isolated from this reaction. One of these, having m. p. about 213°, was not obtained crystalline and therefore was not analysed. Since, however, it gave the original diamine on hydrolysis, it was probably the tetrasulphonyl derivative. The other crystallised from methyl alcohol in needles, m. p. 153—154°, and proved to be a *trisulphonyl* derivative, probably having the constitution (II).

The α-disulphonamide is readily methylated by methyl sulphate in the presence of alkali, yielding NN'-*dimethyldi*-p-*toluenesulphonyl*-2-*phenylnaphthylene*-1 : 3-*diamine*, which, on hydrolysis, yields the β-dimethyldiamine in theoretical amount. This is the most convenient method for preparing the pure β-hase in quantity.

The important investigations by Kenner and his collaborators (J., 1922, **121**, 614 and subsequent papers) on the resolution of substituted diphenylcarboxylic acids have shown that, whilst the molecular asymmetry necessitates the impossibility of free rotation of the two benzene nuclei, the formula suggested by Kaufler to account for certain supposed cases of isomerism is unnecessary (compare Le Fèvre and Turner, J., 1926, 2476). It is significant that molecular asymmetry has been realised only in diphenyl derivatives which have at least three of the four positions

(2 : 2′ : 6 : 6′) substituted and it appears that the substituents should be large (*e.g.*, Cl, NO_2, CO_2H). An adequate explanation of this has been suggested by Mills (*Chem. and Ind.*, 1926, **45**, 883, 905) on a purely mechanical basis (compare Turner and Le Fèvre, *ibid.*, p. 831).

From formula (1), it is clear that in the two *NN′*-dimethyl derivatives of 2-phenylnaphthylene-1 : 3-diamine we have substituted derivatives of diphenyl each with all the substituents in one nucleus. It was found on preparing a model, using ordinary atomic diameters as indicated by Mills (*loc. cit.*), that free rotation of the unsubstituted phenyl group in the dimethyl base is prevented owing to interlocking if all the nuclei and the substituent groups are co-planar. In the light of Mills's suggestion, therefore, it seemed not improbable that one or both forms of this base should be resolvable into optically active forms.

The salts of both α- and β-*NN′*-dimethyl-2-phenylnaphthylene-1 : 3-diamine with optically active acids did not prove satisfactory for the purpose and no evidence of resolution of either of the bases was obtained. We therefore investigated the methylenecamphor derivatives prepared by condensation of each of the two bases with *d*-hydroxymethylenecamphor—a method which, in the hands of Pope and his collaborators (Pope and Read, J., 1913, **103**, 1516; Kipping and Pope, J., 1926, 494), has proved of great value for the optical resolution of primary and secondary amines.

The α-base, when treated with *d*-hydroxymethylenecamphor, gave a quantitative yield of α-NN′-*dimethyl-2-phenylnaphthylene-1 : 3-diaminomono*-d-*methylenecamphor*, only one of the secondary amino-groups reacting. This substance, which crystallised well, was perfectly homogeneous and there was no sign of the formation of optical isomerides. The remaining secondary amino-group is singularly unreactive and cannot be acetylated by acetic anhydride. This abnormal behaviour of the α-dimethyldiamine is exhibited in other reactions, since it only yields a *monoacetyl* and a *mono*-p-*toluenesulphonyl* derivative.

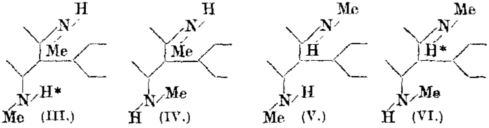
Similar interaction of the β-base with *d*-hydroxymethylenecamphor resulted in the formation of a very sparingly soluble *dimethylenecamphor* derivative, which, like the mono-derivative of the α-base, showed no signs of heterogeneity. The difference in reactivity of the α- and β-bases was further exemplified by the β-base readily yielding a diacetyl derivative and the disulphonamide (m. p. 305°) referred to above.

Although the possibility of the resolvability of the α- and β-dimethyldiamines (compare Gibson and Simonsen, J., 1915, **107**, 115) is not excluded, the facts so far established are adequately explained

by assuming *cis-trans* isomerism of the two bases. This being so the conversion of the one form into the other should be possible We have succeeded in converting the α-form into the β-form by ar indirect method.

Lees and Thorpe showed that both bases yielded dinitrosoamines on treatment with nitrous acid, the formation taking place very slowly from the α-base (*loc. cit.*, p. 1286) and immediately from the β-base. According to these authors (pp. 1298, 1299) the dinitrosoamine prepared from the α-base has m. p. 174—175°, that from the β-base, m. p. 179°; we have now found that these two dinitrosoamines are identical and, when carefully purified, both have m. p. 180—181°. This identity was confirmed by the method of Sidgwick When the dinitrosoamine prepared from either of the bases is reduced with tin and hydrochloric acid, it gives a quantitative yield of the β-dimethyldiamine, and it follows, therefore, that it is the dinitrosoamine of the β-base. This explains the retarded separation of the dinitrosoamine when prepared from the α-base, the course of the change probably being the conversion of the mononitrosoamine of the α-base, which is obviously the first product of the reaction, into the mononitrosoamine of the β-base, followed by formation of the dinitrosoamine. This is in complete accord with the facts that the α-base only yields monoacetyl, mono-*p*-toluenesulphonyl, and monomethylenecamphor derivatives.

The conversion of the α-dimethyldiamine into the β-dimethyldiamine by the nitrosoamine reaction strongly supports the view that these two bases are *cis-trans*-isomerides of a type not previously observed. There would appear to be four possible formulæ (partly represented by III—VI) for these bases on the assumption that the rings and nitrogen atoms with attached groups are co-planar.



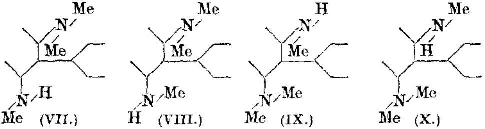
(III.) (IV.) (V.) (VI.)

There can be little doubt that the β-dimethyldiamine must be represented by the *trans*-form (IV), since both the hydrogen atoms of the secondary amino-groups are highly reactive. It is further clear that (V) cannot represent the α-dimethyldiamine, since in it both hydrogen atoms might be expected to be subject to steric hindrance. We have no means of distinguishing between the formulæ (III) and (VI), in each of which one of the hydrogen atoms,

H*, would appear to be likely to be affected by steric hindrance; but we prefer (III), since the base is more reactive than would be anticipated if the hydrogen were in the 1-position in the naphthalene nucleus.

Pending further investigation of related compounds, the suggested uniplanar configuration of the two *NN'*-dimethyldiamines adequately explains their *cis-trans* isomerism. The evidence so far accumulated lends additional support to the generally accepted view that the valencies of a tervalent nitrogen atom lie in one plane.

Lees and Thorpe (*loc. cit.*, p. 1299) described a trimethyldiamine, and we have obtained this base in a somewhat higher state of purity (see p. 2139). It can obviously be represented by partial formulæ (VII—X).



(VII.) (VIII.) (IX.) (X.)

Since this base can be acetylated readily and is also formed by the direct methylation of the β-dimethyldiamine, we consider that it is most probably represented by (VIII). We had hoped to prepare one of the other possible trimethyl bases by the methylation of the α-dimethyldiamine or its *p*-toluenesulphonyl derivative, but in this we were not successful. In alkaline solution the diamine is not methylated, and it is converted into the tetramethyl base by methyl sulphate at 110°. The *p*-toluenesulphonyl derivative was very resistant and was not attacked by methyl sulphate at 145°; above this temperature sulphur dioxide was evolved and decomposition commenced.

EXPERIMENTAL.

2-Phenylnaphthylene-1 : 3-*diamine* was prepared by the method of Lees and Thorpe (*loc. cit.*, p. 1287). We found it advantageous to interrupt the steam distillation as soon as the xylene had passed over, the excess of nitrile being allowed to remain in the distillation flask. The yield of the base was approximately 50% and after crystallising six times from alcohol and once from light petroleum it had m. p. 113·5° (Lees and Thorpe give 116°). The acetyl *acetate*, prepared by boiling the base with acetic anhydride containing a trace of pyridine, crystallised from alcohol in prisms, m. p. 175°. The m. p. 185° given by Atkinson and Thorpe (J., 1906, **89**, 1935) is possibly a misprint (Found: C, 71·3; H, 5·8. Calc.: C, 71·4; H, 5·9%).

α-NN'-Dimethyl-2-phenylnaphthylene-1 : 3-diamine.—The yield of the methylated base was somewhat improved by the following modification of Lees and Thorpe's method. The base (15 g.) was dissolved in methyl alcohol (200 c.c.) and after the addition of methyl sulphate (150 g.) potassium hydroxide solution (600 c.c.; 25%) was added gradually, the temperature being kept below 5° and the mixture mechanically stirred. The crude granular methylation product was dried and boiled with methyl alcohol (50 c.c.), which dissolved the bulk of the impurities. The residue after two crystallisations from light petroleum (b. p. 80—100°) had m. p. 168° (yield, 30%).

As shown by Lees and Thorpe, the base is dimorphic, being obtained either in needles or in prisms according to the conditions of crystallisation. The long needles are obtained most readily if either an alcoholic or light petroleum solution of the base be allowed to crystallise at 30°. If such a solution is allowed to crystallise in the ice-chest, the prism form separates. At 17° the colourless needles become yellow and opaque and are seen under the microscope to be pseudomorphs composed of minute prisms. These gradually pass into large yellow prisms. Both forms have m. p. 170°.

The methyl alcoholic and light petroleum solutions from which the α-base had been obtained gave on removal of the solvents a somewhat gummy residue. This was repeatedly crystallised from alcohol and large colourless prisms were ultimately obtained, m. p. 122° (yield, 35%). This substance was identified as the tetramethyl derivative of the diamine by analysis (Found: N, 9·7. Calc.: N, 9·6%), by the method of mixed m. p., and by conversion into the nitroso-derivative, m. p. 135°.

In another experiment the solid from the mother-liquor was dissolved in hydrochloric acid and treated with sodium nitrite solution. A portion of the nitrosoamines formed was soluble in acid and was identified as the nitrosoamine of the trimethyldiamine (yield, 6%). The crude insoluble nitrosoamine, on reduction with tin and hydrochloric acid, gave, in addition to a resin which was insoluble in acids, a quantity of β-*NN'*-dimethyl-2-phenylnaphthylene-1 : 3-diamine. This was best purified by distillation in superheated steam (yield, 25%).

Methylation of α-NN'-Dimethyl-2-phenylnaphthylene-1 : 3-diamine.—When the α-base was heated for 1 hour at 100° or 115° with an excess of freshly distilled methyl sulphate, the mixture gradually became solid and yielded the tetramethyldiamine, m. p. 122°, in a theoretical yield. The diamine could not be further methylated by treatment with methyl sulphate in alkaline solution.

Monoacetyl-α-NN'-dimethyl-2-phenylnaphthylene-1 : 3-diamine was

obtained when the α-base was digested for some hours with acetic anhydride. It crystallised from alcohol in iridescent prisms, m. p. 203° (Found : N, 9·3. $C_{20}H_{22}ON_2$ requires N, 9·2%).

p-*Toluenesulphonyl-α-NN′-dimethyl-2-phenylnaphthylene*-1 : 3-*diamine*.—A solution of the base (2 g.) and *p*-toluenesulphonyl chloride (5 g.) in pyridine (15 c.c.) was heated on the water-bath for 4 hours, and poured into water. The white solid (3·2 g.) obtained crystallised from alcohol, in which it was somewhat sparingly soluble, in needles, m. p. 219—220° (Found : C, 72·2; H, 5·8. $C_{25}H_{24}O_2N_2S$ requires C, 72·2; H, 5·8%). The *monosulphonamide* was soluble in concentrated hydrochloric acid, and when hydrolysed with a mixture of acetic and sulphuric acids the original α-base was regenerated. It could not be acetylated or methylated, being unaffected by methyl sulphate at 145°.

α-*NN′-Dimethyl-2-phenylnaphthylene*-1 : 3-*diaminomono*-d-*methylenecamphor*.—The α-base (2·6 g.) was dissolved in a mixture of alcohol (140 c.c.) and acetic acid (25 c.c.) and after the addition of *d*-hydroxymethylenecamphor (5·4 g.) in alcohol (15 c.c.) the mixture was heated on the water-bath for 30 minutes. On cooling and dilution with water a crystalline solid (2·7 g.), m. p. 168°, separated and a further quantity (1·7 g.) was obtained from the mother-liquor after treatment with alkali to remove the excess of *d*-hydroxymethylenecamphor. The product, which was quite homogeneous, crystallised from methyl alcohol, in which it was somewhat readily soluble, in colourless prisms, m. p. 167—168°. It depressed the m. p. of the original α-base (Found : N, 6·7. $C_{29}H_{32}ON_2$ requires N, 6·6%*). In alcohol at 20° ($c = 0·2484$, $l = 4$), it gave $\alpha_{5461} = +4·04°$, whence $[\alpha]_{5461} = +406·5°$.

Attempts to prepare an acetyl derivative by treatment with acetic anhydride were unsuccessful.

The salt which formed when equivalent quantities of α-*NN′*-dimethyl-2-phenylnaphthylene-1 : 3-diamine and *d*-camphor-10-sulphonic acid were mixed in hot aqueous alcohol and the mixture allowed to cool separated in glistening prisms and was homogeneous.

The α-base (3·5 g.) was added to a hot solution of *d*-α-bromocamphor-π-sulphonic acid (8·52 g.) in water (445 c.c.), and alcohol (30 c.c.) added to give a clear solution. A voluminous mass of fine needles separated and after 2 days changed to yellow prisms of the α-base, which were optically inactive. The filtrate, on evaporation to dryness in a vacuum over sulphuric acid, gave a deep red resin which slowly crystallised in nodules on being kept in acetone–ethyl

* We are indebted to Mr. A. Bennett, of the Microanalytical Laboratory, University of Manchester, for the microanalyses of this compound and of the dimethylenecamphor compound described on p. 2140.

acetate. The salt, which appeared to be homogeneous, could not be recrystallised, since it was insoluble in acetone, ethyl acetate, benzene, and light petroleum. It was readily soluble in water or alcohol but underwent hydrolysis in these solvents.

β-NN'-*Dimethyl-2-phenylnaphthylene*-1 : 3-*diamine*.—(1) The base (10 g.), heated with methyl sulphate (65 g.) at 100° for 2 hours, gave a solid which had m. p. 93° after crystallisation from alcohol and was evidently a mixture. When the reaction was carried out at 115—120°, an almost theoretical yield of the tetramethyldiamine, m. p. 122°, was obtained and this was characterised by conversion into the nitroso-derivative, m. p. 136°. A series of experiments was carried out at temperatures between 90° and 100°, since it was found that below 90° the product contained much unchanged primary amine. At 90°, the dimethyl derivative was the main product. It was found possible to estimate fairly accurately the percentages of dimethyl and trimethyl derivatives in the product by treatment with nitrous acid, since the mononitrosoamine of the trimethyl base was soluble in mineral acids, and the dinitrosoamine of the dimethyl base insoluble. The results are in the following table, 2 g. of the crude methylation product being used in each case.

Temp. of methylation.	Dinitroso-amine.	Mononitroso-amine.	% Me_2.	% Me_3.
90°	2·12 g.	0·24 g.	87	11
94	1·20	1·11	49	50
100	0·73	1·55	30	70

(2) The β-base was prepared in quantity by the methylation of *di-p-toluenesulphonyl-2-phenylnaphthylene*-1 : 3-*diamine*, followed by hydrolysis. A solution of the diamine (50 g.) and *p*-toluenesulphonyl chloride (150 g.) in pyridine (400 c.c.) was heated on the water-bath for 4 hours and poured into water. The thick brown oil obtained was washed with dilute hydrochloric acid to remove pyridine and heated on the water-bath for 30 minutes with sodium carbonate solution to remove the excess of acid chloride; the remainder solidified on cooling and then had m. p. 175—183° (yield, 14 g.). It was best purified by solution in sodium hydroxide (10%), which left undissolved a small quantity of a red solid (*A*). When the filtrate was acidified the sulphonamide was deposited as an almost colourless, crystalline powder. It was recrystallised from alcohol, α-*di-p-toluenesulphonyl-2-phenylnaphthylene*-1 : 3-*diamine* being obtained pure; the mother-liquor contained a small quantity of a second substance (see below).

The sulphonamide was dimorphic. When crystallised from methyl alcohol, the α-form separated in fine glistening prisms, m. p. 203—205°, and the same form resulted if the amide was allowed to

separate from a *hot* solution in either alcohol or acetic acid. If this form was crystallised from a dilute solution in alcohol, so that deposition took place in the cold, prisms were also obtained which had, however, m. p. 188—189°, rapidly resolidified, and then melted at 203—205°. This low-melting α_1-form was also obtained when an alkaline solution of the sulphonamide was acidified (Found: for α, C, 66·4; H, 4·9; for α_1, S, 12·0. $C_{30}H_{26}O_4N_2S_2$ requires C, 66·4; H, 4·8; S, 11·8%). The sulphonamide was somewhat sparingly soluble in alcohol, benzene, and acetic acid and insoluble in water and light petroleum. The dimorphic relationship of these two forms was established by Sidgwick's method (*loc. cit.*) with benzene as the solvent, the following depressions being observed:

Depression of f. p. by α_1 alone	0·086°
,, ,, ,, ,, α ,,	0·025
,, ,, ,, ,, $\alpha + \alpha_1$	0·029

The original mother-liquor from the first crystallisation of the sulphonamide contained a small quantity of a second substance which, after repeated crystallisation from methyl alcohol, in which it was somewhat readily soluble, was obtained in soft needles, m. p. 173—175°. It is possible that this m. p. is not quite accurate, since the amount of material available for purification was small (Found: C, 66·8; H, 4·9. $C_{30}H_{26}O_4N_2S_2$ requires C, 66·4; H, 4·8%). β-*Di*-p-*toluenesulphonyl*-2-*phenylnaphthylene*-1 : 3-*diamine* is much more readily soluble in the ordinary organic solvents than either of the α-forms and when mixed with these causes a marked depression in m. p.

The solid (*A*) (see above), which was insoluble in alkali, dissolved in hot alcohol, yielding a deep red solution from which a brown amorphous solid, m. p. about 213°, was slowly deposited. This product could not be obtained pure enough for analysis, but was probably the tetrasulphonyl derivative of the diamine, since on hydrolysis with a mixture of acetic and sulphuric acids it gave the original base. The deep red mother-liquor on concentration yielded a small quantity of a crystalline solid, which after repeated crystallisation from methyl alcohol was obtained in fine, colourless needles, m. p. 153—154°. Analysis showed this to be *tri*-p-*toluenesulphonyl*-2-*phenylnaphthylene*-1 : 3-*diamine* (II) (Found: C, 63·7; H, 4·6. $C_{37}H_{32}O_6N_2S_3$ requires C, 63·8; H, 4·6%).

Di-p-*toluenesulphonyl*-NN′-*dimethyl*-2-*phenylnaphthylene*-1 : 3-*diamine*.—The α-disulphonamide (50 g.) was dissolved in sodium hydroxide solution (270 c.c.; 10%) and methyl sulphate (200 c.c.) was added gradually with constant agitation, the solution being kept alkaline. An oil separated which rapidly solidified (53 g.); it

crystallised from pyridine in small plates, m. p. 305° (Found: C, 67·5; H, 5·3. $C_{32}H_{30}O_4N_2S_2$ requires C, 67·3; H, 5·3%). The methyl derivative was very sparingly soluble in all the ordinary organic solvents.

*Hydrolysis of Di-*p*-toluenesulphonyl-*NN′*-dimethyl-2-phenylnaphthylene-*1 : 3*-diamine.*—The amide (100 g.) was dissolved in a mixture of acetic acid (100 c.c.) and sulphuric acid (200 c.c.) and heated on the water-bath for 2 hours. The clear brown solution was poured on ice and made alkaline with ammonia. An oil separated which rapidly solidified (yield, 46 g.); after crystallisation from alcohol it had m. p. 159—160° and was pure β-*NN′*-dimethyl-2-phenylnaphthylene-1 : 3-diamine. When this base was treated with *p*-toluenesulphonyl chloride in pyridine solution, it was reconverted into the above-mentioned sulphonamide, m. p. 305°. On treatment with methyl sulphate at 100° it was converted quantitatively into the tetramethyl base, m. p. 122°, and in alkaline solution it was partly converted into the trimethyldiamine, which was identified by the preparation of the nitrosoamine.

*Diacetyl-*β-NN′*-dimethyl-2-phenylnaphthylene-*1 : 3*-diamine.*—The β-base was boiled for 2 hours with acetic anhydride, and after removal of the excess of the anhydride by evaporation with alcohol the *acetyl* derivative was recrystallised from dilute methyl alcohol or benzene and obtained in rosettes of small prisms, m. p. 207—208° (Found: N, 8·2. $C_{22}H_{22}O_2N_2$ requires N, 8·1%).

β-NN′*-Dimethyl-2-phenylnaphthylene-*1 : 3*-diaminodi-*d*-methylenecamphor.*—The β-base (2·6 g.) was dissolved in a mixture of alcohol (75 c.c.) and acetic acid (20 c.c.; 50%) and after the addition of *d*-hydroxymethylenecamphor (5·4 g.) in alcohol (15 c.c.) the mixture was heated on the water-bath for 30 minutes. On cooling in the ice-chest over-night, a hard, crystalline cake (4·25 g.), m. p. 274—277°, had separated. By evaporation of the filtrate and removal of the excess of *d*-hydroxymethylenecamphor with alkali a further quantity (1·6 g.) was obtained. It crystallised from alcohol in nodules of colourless prisms, m. p. 277—279° (Found: N, 5·2. $C_{40}H_{46}O_2N_2$ requires N, 4·8%). In alcohol at 20° ($c = 0·2142$, $l = 4$), it gave $\alpha_{5461} = +5·57°$, whence $[\alpha]_{5461} = +650·1°$.

The β-base (2 g.) was added to a hot solution of *d*-camphor-10-sulphonic acid (3·54 g.) in water (7 c.c.). On cooling, the viscid, red solution deposited a mass of fine needles. This salt dissolved in its own water of crystallisation at 105° and was very readily soluble in water, acetone, and alcohol, less soluble in ethyl acetate. The salt and the mother-liquor were separately made alkaline; the base recovered was in each case optically inactive.

The β-base (2 g.), when added to a hot solution of *d*-β-bromo-

camphor-π-sulphonic acid (4·74 g.) in water (25 c.c.), slowly dissolved, giving a reddish-brown solution which deposited an oil on stirring. On cooling, the oil redissolved, but there was no separation of crystals. The solvent was evaporated in a vacuum and the residual resin, which was readily soluble in acetone, crystallised slowly from a solution in ethyl acetate. It was recrystallised from acetone–ethyl acetate, from which it was deposited in nodules. The bases recovered from the crystalline salt and from the mother-liquor were inactive.

The Dinitrosoamines of α- and β-NN′-Dimethyl-2-phenylnaphthylene-1 : 3-diamines.—α-Base. The dinitrosoamine was prepared as described by Lees and Thorpe (*loc. cit.*, p. 1297) and obtained in a yield of 85%. After recrystallisation from alcohol and then from benzene, it was obtained in clusters of yellow needles, m. p. 180°.

β-Base. The dinitrosoamine was obtained from the β-base in a somewhat better yield (95%). The final crystallisation was from benzene. It had m. p. 180—181°.

These two dinitrosoamines were found to be identical. They have the same m. p. and mixtures in all proportions melt at this temperature. The identity was confirmed by the application of Sidgwick's method (*loc. cit.*), benzene being used as the solvent. The following depressions were observed :

Depression of f. p. with	β-form alone, 0·759°
,, ,, ,, ,,	β- + α-forms, 0·764
,, ,, ,, ,,	α-form alone, 0·750
,, ,, ,, ,,	α- + β-forms, 0·761

NN′-*Trimethyl-2-phenylnaphthylene-*1 : 3-*diamine.*—The crude nitrosoamine of the trimethyl base obtained by the action of methyl sulphate on the diamine (see p. 2136) crystallised from alcohol in buff-coloured needles, m. p. 151°. These (5 g.) were dissolved in acetic acid (25 c.c.) and, after the addition of an excess of tin and hydrochloric acid, heated on the water-bath for ½ hour, the red solution rapidly becoming colourless. The solution was made alkaline with sodium hydroxide, boiled to decompose tin salts, and extracted with benzene. The dried benzene solution was evaporated, leaving the colourless base, which crystallised from alcohol in needles, m. p. 104—105° (Lees and Thorpe, *loc. cit.*, give 98—99°) (yield, 4·4 g.) (Found : C, 82·8; H, 7·3. Calc. : C, 82·6; H, 7·2%).

The *acetyl* derivative, prepared by means of acetic anhydride, crystallised from alcohol in needles, m. p. 178° (Found : N, 9·0. $C_{21}H_{22}ON_2$ requires N, 8·8%).

One of us (W. S. K.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant which has enabled

him to take part in the work. We wish to express our thanks to the Government Grant Committee of the Royal Society for a grant which has defrayed the greater part of the cost of this investigation.

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CCLXXXI.—*The Interaction of Cuprous Chloride and the Chromates of Potassium in a Solution of Sodium Chloride.*

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ROSENFELD (*Ber.*, 1879, **12**, 958) obtained a green precipitate on adding cuprous chloride, dissolved in a concentrated solution of sodium chloride, to an excess of a solution of potassium chromate. Similar experiments are now described, and, in addition, the dichromate was used, and the order in which the reagents were mixed was sometimes reversed. Complex precipitates were obtained, differing in colour and constitution according to the method of preparation. The reaction is shown to consist essentially in the oxidation of the cuprous salt and reduction of the chromate or dichromate, with formation of basic compounds, but owing to their instability to washing, these compounds do not always give trustworthy analytical results.

EXPERIMENTAL.

Materials.—Cuprous chloride, prepared by the method of Wöhler (*Ann. Chem. Pharm.*, 1864, **130**, 373), was stored in the dark in a vacuum desiccator, and remained quite white indefinitely (Found: Cu, by iodometric method, 64·11, 64·06; by electrolysis, 64·08. Calc.: Cu, 64·10%). The other reagents were of A.R. quality; the chromate and dichromate were recrystallised twice and thoroughly dried. All solutions were made up free from dissolved air and stored under hydrogen, and all the experiments were carried out in an atmosphere of the same gas.

Apparatus.—This consisted of a wide-necked bottle, of about 1 l. capacity, fitted with a rubber stopper carrying a motor-driven stirrer, an inlet tube for hydrogen, and a burette.

The reactions were all carried out at room temperature, except in Case II, and the theoretical values in the tables are based on equations (1)—(4) on p. 2145.

Case I. When a dilute solution of potassium dichromate is slowly added to cuprous chloride dissolved in concentrated sodium

chloride solution, a green precipitate is continuously formed until the whole of the chloride is oxidised. If the dichromate is added too rapidly, some of it reacts with the basic products, which then become contaminated with a basic chromate. If this side reaction is avoided, reaction takes place in the molecular ratio $Cu_2Cl_2 : K_2Cr_2O_7 = 3 : 1$, for when known amounts of each reagent were used, complete analyses of the precipitates and filtrates gave the following values for this ratio: 2·96, 3·02, 2·99, 2·99.

Known weights of cuprous chloride were oxidised by the addition during 5 hours of the calculated volumes of a 1% solution of potassium dichromate; cupric chloride was estimated in the filtrate, the amounts of copper thus found being given below as a percentage of the cuprous chloride taken.

G. of Cu_2Cl_2 taken (approx.).	Conc. of sodium chloride solution used. 15%.	20%.	25%.
1	5·64% Cu	5·30% Cu	5·67% Cu
2·5	—	5·79	—
5	5·84	5·45	5·33

Average 5·57% Cu; theory requires 5·35% Cu.

The washed precipitates were dried to constant weight at 97°, and their analyses are given in Table I.

TABLE I.

	1.	2.	3.	4.	5.	6.	Mean.	Calc.	Atomic ratios, found.	theory.
Cu, %	43·00	42·92	42·80	42·85	42·82	42·85	42·87	42·38	11	11
Cr, %	12·85	—	—	—	12·83	12·83	12·84	12·61	4·03	4
Cl, %	—	12·90	—	13·04	—	13·05				
Cl, % (corr.)*		12·60		12·55		12·50	12·52	12·89	5·77	6
H_2O, %	18·80	—	—	18·70	—	—	18·75	18·57		

* The correction is due to the deduction of chlorine present in the precipitate as sodium chloride.

Case II. When an attempt was made to oxidise cuprous chloride with potassium chromate in the same way, the reaction did not go to completion, although different conditions of concentration, time of stirring, and temperature (up to 60°) were tried. In two cases the partial precipitates were filtered off, washed, dried at 97°, and analysed:

	1.	2.	Atomic ratios, for 1.	for 2.	theory.
Cu, %	48·04	32·09	6	6	6
Cr, %	13·67	9·53	2·09	1·69	2
Cl, %	10·30	—	2·25	—	2

Case III. Known quantities (1·0—1·5 g.) of cuprous chloride were dissolved in 500 c.c. of 20% sodium chloride solution and added

more or less rapidly to excess of potassium dichromate solution; brown precipitates were immediately produced, and the filtrates contained cupric chloride (Found: Cu, as % of Cu_2Cl_2 taken, 10·84, 10·80. Calc.: Cu, 10·70%). The precipitates were washed, and dried at 97°. They contained the chromate radical, but no chlorine. The analyses are given in Table II.

TABLE II.

	1.	2.	3.	Mean.	Calc.	Atomic ratios, found.	Atomic ratios, theory.
Cu, %	36·30	36·42	36·44	36·38	36·30	5	5
Cr, %	11·60	11·70	11·75	11·68	11·87	1·96	2
CrO_4 as % Cr	11·71	11·78	11·76	11·75	11·87	1·97	2
H_2O, %	14·58	14·50	—	14·54	14·40		

Although the precipitate obtained in Case I reacts with potassium dichromate, we have satisfied ourselves that, even on digestion with 1% potassium dichromate solution for 2—5 days, it cannot be made to yield a precipitate of the same composition as that obtained in Case III, for under such conditions the average composition of the final product, dried at 97°, was Cu, 37·86; Cr, 13·12; Cr, present as CrO_4, 8·15; Cl, 10·25%. It will be seen that although a large percentage of chromate radical is now present, very little change has taken place in the ratio Cu : Cl.

Case IV. These experiments were carried out in the same way as those in Case III, potassium chromate being used instead of the dichromate. This was a repetition of Rosenfeld's (*loc. cit.*) experiment, as far as could be gathered from the available details. The washed precipitates were dried at 110°, as in his experiments, and the results are shown in Table III. Our figures are in better agreement, among themselves, than Rosenfeld's, and the atomic ratios agree better with equation (4) than do those obtained from his results.

TABLE III.

	1.	2.	3.	Mean.	Calc.	*Atomic ratios,* found.	*Atomic ratios,* theory.
Cu, %	43·55	43·50	43·64	43·56	43·65	6	6
Cr, %	11·60	11·72	11·70	11·67	11·91	1·97	2
CrO_4 as % Cr	6·14	6·01	6·13	6·09	5·95	1·03	1
Total Cr, %	17·74	17·73	17·83	17·76	17·86	3·00	3
H_2O, %	16·01	—	16·62	16·31	16·50		

Discussion.

It is noteworthy that, in spite of variations in the concentration of the sodium chloride solution and of casual alterations in the time and other conditions, the analytical results are so constant for each set of experiments. Another point of interest is the fact that the reagents are not used up in every case in the proportions given by

the simplest equations by which the reactions can be expressed, *viz.*, (5) and (6). The results of the analyses show that further reactions have taken place, and we give below equations for these secondary reactions. Equations (1), (2), (3), and (4) express, for the respective cases, the sum of all the reactions, and it is from these equations that the theoretical values in the tables have been calculated.

For Case I.

$2(3Cu_2Cl_2 + K_2Cr_2O_7 + 7H_2O) = 2[2KCl + 2CuCl_2 + 4Cu(OH)_2 + 2Cr(OH)_3]$ . . . . . . (5a)

$CuCl_2 + 2Cu(OH)_2 + H_2O = 2CuO,CuCl_2,3H_2O$.

$2CuCl_2 + 6Cu(OH)_2 + 2H_2O = 2(3CuO,CuCl_2,4H_2O)$

or $6Cu_2Cl_2 + 2K_2Cr_2O_7 + 17H_2O = 4KCl + CuCl_2 + 2CuO,CuCl_2,3H_2O + 2(3CuO,CuCl_2,4H_2O) + 4Cr(OH)_3$ . . . . (1)

For Case II.

$3Cu_2Cl_2 + 2K_2CrO_4 + 8H_2O = 4KCl + CuCl_2 + 5Cu(OH)_2 + 2Cr(OH)_3$ . . . . (6)

$CuCl_2 + 3Cu(OH)_2 = 3CuO,CuCl_2,3H_2O$

or $3Cu_2Cl_2 + 2K_2CrO_4 + 8H_2O = 4KCl + 3CuO,CuCl_2,3H_2O + 2Cu(OH)_2 + 2Cr(OH)_3$ . . (2)

For Case III.

$3Cu_2Cl_2 + K_2Cr_2O_7 + 7H_2O = 2KCl + 2CuCl_2 + 4Cu(OH)_2 + 2Cr(OH)_3$ . . . . (5)

$Cu(OH)_2 + K_2Cr_2O_7 = CuCrO_4 + K_2CrO_4 + H_2O$

$K_2CrO_4 + CuCl_2 = CuCrO_4 + 2KCl$

$2CuCrO_4 + 3Cu(OH)_2 + H_2O = 3CuO,2CuCrO_4,4H_2O$

or $3Cu_2Cl_2 + 2K_2Cr_2O_7 + 7H_2O = 4KCl + CuCl_2 + 3CuO,2CuCrO_4,4H_2O + 2Cr(OH)_3$ . . . . (3)

For Case IV.

$3Cu_2Cl_2 + 2K_2CrO_4 + 8H_2O = 4KCl + CuCl_2 + 5Cu(OH)_2 + 2Cr(OH)_3$ . . . . (6)

$CuCl_2 + K_2CrO_4 = 2KCl + CuCrO_4$

$CuCrO_4 + 2Cu(OH)_2 = 2CuO,CuCrO_4,2H_2O$

or $3Cu_2Cl_2 + 3K_2CrO_4 + 8H_2O = 6KCl + 2CuO,CuCrO_4,2H_2O + 3Cu(OH)_2 + 2Cr(OH)_3$. (4)

Chromates of chromium have been intentionally ignored, on account of the doubt as to their existence in presence of water. The basic chlorides and chromates of copper given above are all known, except $3CuO,2CuCrO_4,4H_2O$; Rosenfeld (*Ber.*, 1880, **13**, 1470), however, has described the compound $5CuO,2CuCrO_4,5H_2O$.

The compound $3CuO,CuCl_2,4H_2O$ has been characterised by Britton (J., 1925, **127**, 2803).

In the equations for the secondary reactions, cupric hydroxide is imagined as behaving at the moment of formation like an electrolyte, *and this supposition explains the interesting fact that the reaction* proportions and products vary with the manner of mixing the reactants.

Summary.

(1) The interactions of cuprous chloride, dissolved in a solution of odium chloride, with potassium chromate and dichromate have een studied.

(2) The colour and composition of the precipitates formed lepend on the chromate used and on the manner of precipitation.

(3) The precipitates have been analysed, and equations involving asic copper salts have been proposed, according to which the ormation of these basic salts is ascribed to secondary reactions.

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CLXXXII.—*Acid and Salt Effects in Catalysed Reactions. Part XV. The Catalytic Activity of Hydrochloric Acid in the Hydrolysis of Ethyl Acetate.*

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HE experiments to be described in this paper represent an attempt measure as accurately as possible the catalytic effect produced y hydrochloric acid of widely varying concentration in the ydrolysis of ethyl acetate.

If the active mass of the hydrolyte is constant and the catalytic fect is assumed to be due to the hydrogen ion, then according to e classical theory the reaction velocity should be given by the uation $v = kc_H$. On the other hand, the equation for the velocity cording to the activity theory is $v = k'a_H = k'f_H . c_H$ in which the tivity coefficient f_H varies with the hydrogen-ion concentration, , more generally, with the ionic concentration of the reaction edium.

According to Brönsted (*Z. physikal. Chem.*, 1922, **102**, 169; 1925, **15**, 337), these equations are particular forms of a more general uation, for the applicability of which a substantial amount of perimental evidence has been brought forward. In terms of is equation, the influence of the ionic environment which is

expressed by f_H depends on the nature of the primary reaction. f this involves the interaction of the hydrogen ion with a neutral nolecule, the reaction velocity should not be greatly affected by he ionic concentration of the reaction medium, but the converse vould be true if the primary change involves the interaction of the ıydrogen ion with a negatively charged entity.

For certain reactions, it may not be difficult to identify with some legree of certainty the constituents which are involved in the rimary change, but this is by no means generally the case. In uch circumstances it cannot be definitely stated whether a given eaction will or will not be markedly affected by variations in the onic environment. This, indeed, is a matter for experiment, and n the consideration of the data yielded by experiments on acid-atalysed reactions it is of the first importance to ascertain whether he observed catalytic effect is simple or composite. This necessi-ates the consideration of the effects which may be produced by ıeutral molecules and negative ions, as well as those which are due o the "hydrogen" or other similar positive ions. Unless due egard is paid to the possibility of such simultaneous catalytic ffects, it is scarcely feasible to discuss the question whether the atalytic activity of the hydrogen ion is proportional to its con-entration, or whether it is dependent on a factor which varies ery appreciably with the ionic concentration of the reaction nedium. Furthermore, since the ionisation constants of weak cids are changed by the addition of catalytically inert salts, it is bvious that any attempt to discriminate between concentration nd "activity" as the factor which determines the catalysing ower of the hydrogen ion requires a careful choice of the experi-ıental conditions. These should be such that the observed atalytic effect can with reasonable certainty be ascribed entirely o the hydrogen ion, and it should further be possible to measure he reaction velocity over a wide range of hydrogen-ion concen-rations, for which range the corresponding variations in the hermodynamic activity should be known with some degree of ertainty.

These considerations suggested hydrochloric acid as a suitable atalyst for investigation, for, on the one hand, there is good reason o suppose that this acid is almost completely ionised in dilute olution and that the catalytic effects produced by it may be ascribed ntirely to the hydrogen ion, and, on the other, the dependence of ıe thermodynamic activity of hydrochloric acid on its concentration as been determined with considerable precision by various methods.

In selecting the hydrolysis of ethyl acetate as an acid-catalysed eaction for which the requisite conditions would appear to be

satisfied, we were also influenced by the circumstance that this reaction had been previously studied with results which were said to support the view that the catalytic effects produced by hydrochloric acid are related to the thermodynamic activity of the hydrogen ion.

The data recorded by Harned and Pfanstiel (*J. Amer. Chem. Soc.*, 1922, **44**, 2193) suggest that the specific catalytic activity of hydrochloric acid passes through a minimum at a concentration of 0·07—0·08 mol. per litre. This minimum is supposed to be connected with a minimum in the activity coefficient of the hydrogen ion, which according to these authors occurs at an acid concentration of 0·15—0·18 mol. per litre.

From a study of the effects produced by the addition of chlorides to a 0·05*N*-hydrochloric acid solution, Åkerlöf (*Z. physikal. Chem.*, 1921, **98**, 260) draws the conclusion that the catalytic activity of the acid is proportional to the cube root of the activity of the hydrogen ion. Such a relation can scarcely be regarded as other than empirical. For other reactions, *e.g.*, the inversion of sucrose (compare Jones and Lewis, *J.*, 1920, **117**, 1120; Moran and Lewis, *ibid.*, 1922, **121**, 1613; Scatchard, *J. Amer. Chem. Soc.*, 1921, **43**, 2387), where the experimental results have been interpreted in terms of the activity of the hydrogen ion, the proof of the alleged relation between reaction velocity and hydrogen-ion activity appears to be equally inconclusive. The conversion of *N*-chloroacetanilide into *p*-chloroacetanilide in presence of hydrochloric acid (compare Harned and Seltz, *J. Amer. Chem. Soc.*, 1922, **44**, 1475; Soper and Pryde, J., 1927, 2761) is not catalysed by hydrogen ions and will not therefore be discussed here.

The evidence for the view that the rate of hydrolysis of ethyl acetate with hydrochloric acid as catalyst is determined by the thermodynamic activity of the hydrogen ion did not seem to us to be acceptable, and for this reason new measurements have been undertaken which extend the previous lower limit for the concentration of the hydrochloric acid from 0·01*N* (compare Taylor, *Medd. K. Vetenskapsakad. Nobel.-Inst.*, 1913, **2**, No. 34; Harned and Pfanstiel, *loc. cit.*) to the much lower value 0·0002*N*.

When the concentration of the hydrochloric acid is less than 0·01*N*, the course of the reaction is markedly affected by the acetic acid produced. This autocatalytic influence of the acetic acid, which increases as the concentration of the hydrochloric acid diminishes, precludes the use of any simple integration formula in the co-ordination of the experimental data. We have therefore attempted to measure directly the velocity of the reaction in the early stages of hydrolysis. These measurements were made at

25° with a fixed concentration of ethyl acetate ($e = 0{\cdot}206$ mol. per litre) in presence of hydrochloric acid varying in concentration from $c = 0{\cdot}0002$ to $c = 0{\cdot}002$ mol. per litre. Carefully selected, chemically inert flasks were used as containers.

In these experiments, the reaction was allowed to proceed until a small proportion (0·5—3%) of the ester was hydrolysed. If Δx denotes the concentration of the acetic acid formed during the interval t, then $\bar{v} = \Delta x/t$ represents the mean velocity for this period, and $x = \Delta x/2$ is the mean concentration of the acetic acid. For the attainment of the primary object of these experiments it was soon realised that the values of x which determine the magnitude of the autocatalytic effect must be kept as small as possible, and this necessitated the carrying out of the observations on a large scale which may be illustrated by reference to the detailed procedure followed in an experiment with $0{\cdot}0005N$-hydrochloric acid. The requisite amount of a $0{\cdot}01N$-hydrochloric acid solution was weighed into a 250 c.c. flask, and freshly distilled water was added to give about 240 c.c. of solution. When the temperature had reached 25°, 5·00 c.c. of ester were added and the volume was made up to 250 c.c. After a suitable interval (about 4 days) the entire contents of the flask were titrated with $0{\cdot}1N$-sodium hydroxide solution. The initial acidity was derived from the immediate titration of a similarly prepared parallel solution. For $t = 5864$ minutes, the titration difference thus obtained was 10·83 c.c., which represents 2·1% hydrolysis and corresponds with $\Delta x = 0{\cdot}00433$, $x = 0{\cdot}00216$, and $\bar{v} = 7{\cdot}38 \times 10^{-7}$ mol. per litre per minute.

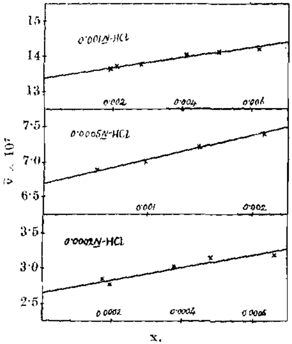
If for small values of x, the magnitude of which depends on the concentration (c) of the hydrochloric acid, the observed mean reaction velocities ($\bar{v}$) are plotted against the corresponding mean acetic acid concentrations (x), a straight line is obtained. By extrapolation to $x = 0$, the autocatalytic effect may be eliminated, and the initial velocity v_0 due to the undisturbed action of the hydrochloric acid may be derived. Since the mean ester concentration $(e - x)$ falls slightly as x increases, more strictly comparable velocities are those given by $\bar{v}' = \bar{v}e/(e - x)$, but as a matter of fact the substitution of $\bar{v}'$ for $\bar{v}$ makes no appreciable difference to the value of the extrapolated initial velocity. The graphs of $\bar{v}$ against x are shown in Fig. 1, and the initial velocities derived from these are $v_0 = 13{\cdot}40 \times 10^{-7}$, $6{\cdot}70 \times 10^{-7}$, and $2{\cdot}65 \times 10^{-7}$ respectively for $c = 0{\cdot}001$, $0{\cdot}0005$, and $0{\cdot}0002$ mol. per litre. From these initial velocities, the values of the catalytic coefficient k are then given by $k = v_0/ce$.

As the concentration of the hydrochloric acid increases, the autocatalytic influence of the acetic acid diminishes rapidly. For

0·002N-hydrochloric acid, the autocatalytic effect is almost exactly counterbalanced by the effect of the fall in the ester concentration, with the result that the observed mean velocity in the early stages of hydrolysis is practically identical with the initial velocity.

In hydrochloric acid solutions more concentrated than 0·01N, the autocatalytic effect may be almost entirely neglected in comparison with the change in the velocity which is due to the fall in the ester concentration, and for these solutions the velocity coefficient has been derived from the formula $k = 1/ct \,.\, \log e/(e - \Delta x)$, having

FIG. 1.



Plot of mean reaction velocity ($\bar{v}$) *against mean acetic acid concentration* (x) *for* 0·001N-, 0·0005N-, *and* 0·0002N-*hydrochloric acid as catalyst.*

due regard for the range over which this is applicable witho appreciable interference from the reverse reaction (compare Daws and Lowson, J., 1927, 2107).

The values of k obtained by the above methods are in Table I.

TABLE I.

c	0·0002	0·0005	0·001	0·002	0·01	0·02	0·04	0·1	0·2	0·[illegible]
$k \,.\, 10^3$	6·43	6·50	6·50	6·49	6·54	6·45	6·50	6·48	6·57	6·[illegible]

In the consideration of these figures, it may be noted that c 0·0002 represents the lowest concentration of hydrochloric a for which it is possible in practice to make use of the linear ex polation method. At greater dilutions, the autocatalytic ef

plays too large a part. For the interval $c = 0{\cdot}0002$—$0{\cdot}2$, the constancy of k, within the limits of experimental error, signifies that the catalytic activity of the hydrochloric acid is proportional to its concentration. Over this range the activity coefficient falls from 0·994 to 0·783 (Lewis and Randall, "Thermodynamics") and the mean activity coefficient from 0·997 to 0·884. According to Harned (*J. Amer. Chem. Soc.*, 1920, **42**, 1818), the fall in the individual activity coefficient of the hydrogen ion is less than this, but the argument on which this conclusion is based seems doubtful. In the circumstances, the mean activity coefficient would seem to afford the only data for comparing the activity and the concentration of the hydrogen ion, and as is evident from the constancy of k in the above table, there is no apparent connexion between the catalytic activity and the thermodynamic activity.

The fact that k increases with c at higher concentrations (compare, *e.g.*, Harned and Pfanstiel, *loc. cit.*) may be due to the action of undissociated hydrochloric acid, which is in all probability a very active catalyst. Ionic effects of the kind associated with catalytically inert salts (compare Dawson and Key, this vol., p. 1239) may also play a part, and it does not yet seem possible to attempt the interpretation of the observations which have been made on the action of hydrochloric acid in concentrated solutions.

The mean reaction velocities used in the above-described method for the elimination of the autocatalytic effect represent only a part of the observations made with dilute hydrochloric acid solutions. Other measurements were made in which the proportion of acetic acid was greater, and prior to the consideration of the experimental data, the catalytic process may be subjected to closer analysis.

In accordance with previous results, the equation for the reaction velocity may be written

$$\begin{aligned} v &= v_h + v_{OH} + v_a + v_w + v_m \\ &= \{k_h[H^+] + k_{OH}[OH^-] + k_a[A^-] + k_w[H_2O] + \\ &\qquad k_m[HA]\} . [\text{ester}][\text{water}] \quad . \quad (1) \end{aligned}$$

Since $k_{OH}/k_h = 10^3$, it follows that the v_{OH} term may be neglected if the hydrogen-ion concentration is greater than 10^{-4}. This was actually the case in all experiments. From the ratios $k_a/k_h = 3{\cdot}3 \times 10^{-5}$ and $k_m/k_h = 2{\cdot}4 \times 10^{-4}$ (Dawson and Lowson, J., 1927, 2444) it is also apparent that v_a and v_m may be neglected in comparison with v_h. The term v_w is probably extremely small, evidence for this view being afforded by the reaction-velocity data for mixtures of the series $0{\cdot}1CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$, which can be satisfactorily interpreted without the introduction of such a term. It would therefore appear that the velocity of hydrolysis under the

conditions of these experiments is determined by the concentration of the hydrogen ion. We may therefore write

$$v = k_h[H^+][\text{ester}][\text{water}] = k[H^+][\text{ester}] \quad . \quad . \quad (2)$$

Furthermore, since $[H^+] = [Cl^-] + [A^-] = c + [A^-]$

and $[A^-] = K(x - [A^-])/(c + [A^-])$

we derive $[H^+] = c + \frac{1}{2}\{\sqrt{(K+c)^2 + 4Kx} - (K+c)\}$ (3)

For such small differences in the concentration of the acetic acid as are involved in the determination of $\bar{v}$, the hydrogen-ion concentration given by (3) and the corresponding reaction velocity given by (2) are linear functions of x. It follows that the observed mean reaction velocity $\bar{v} = \Delta x/t$ should be very nearly identical with the actual velocity due to the catalytic action of the mixture cHCl + xCH$_3$·CO$_2$H, where x is the mean concentration of the acetic acid for the interval t. Equation (2) may therefore be written in the form

$$k = \Delta x/[H^+](c - \tfrac{1}{2}\Delta x)t \quad . \quad . \quad . \quad . \quad . \quad (4)$$

When the values of $[H^+]$ derived from (3) by the introduction of $K = 1{\cdot}85 \times 10^{-5}$ are used to calculate k from (4), it is found that k diminishes slowly as the concentration of the acetic acid increases. This suggests that the ionisation constant of the acetic acid in the ester solution is less than the value for pure aqueous solutions. In view of the fact that the hydrogen-ion concentration of aqueous solutions of weak acids is very appreciably reduced on the addition of substances such as ethyl alcohol, acetone, etc., it may indeed be expected that ethyl acetate, as a substance of low dielectric capacity, will produce a similar and even greater effect. Evidence of this reduction is afforded by the data obtained in the experiments of Dawson and Lowson (*loc. cit.*) on the rate of ester hydrolysis with acetic acid as catalyst, from which the value derived for $k\sqrt{K}$ is $2{\cdot}61 \times 10^{-5}$. Combining this with $k = 6{\cdot}5 \times 10^{-3}$, we obtain $K = 1{\cdot}6 \times 10^{-5}$ for the ionisation constant of acetic acid in a 0·4-molar solution of ethyl acetate.

In qualitative agreement with this result, it has been found that the conductivity (κ) at 25° of a 0·1N-solution of acetic acid in the above solvent (40 c.c. of ester per litre) is only $4{\cdot}57 \times 10^{-4}$ mho as compared with $\kappa = 5{\cdot}30 \times 10^{-4}$ mho when the solvent is pure water. This difference may be due in part to a change in the ionic mobilities, but there can be little doubt that the presence of the ester reduces the ionisation of the acetic acid. In the presence of hydrochloric acid the reduction may be counteracted to some extent as a result of the increase in the ionic concentration in the environment of the dissociable acetic acid molecules, but since the hydro-

chloric acid concentrations concerned are very small, this effect is probably not of much importance. A detailed investigation of the relations in question might enable us to express the ionisation constant as a function of the concentrations of the ester and of the hydrochloric acid, but the necessary data are not available. In these circumstances the ionisation constant has tentatively been given the value $K = 1{\cdot}6 \times 10^{-5}$, in terms of which it is possible, as will be shown, to give a satisfactory account of the observed reaction velocities.

The results are summarised in Table II. Col. 1 gives the time intervals in minutes; Col. 2 the quantities of ester in mols. per litre hydrolysed during these intervals; Col. 3 the mean reaction velocities $\Delta x/t \, . \, 10^7$; Col. 4 the mean ester concentrations $(e - \Delta x/2)$; Col. 5 the mean acetic acid concentrations $(x \, . \, 10^3)$; Col. 6 the mean hydrogen-ion concentrations $[H^+] \, . \, 10^3$; and Col. 7 the velocity coefficients $(k \, . \, 10^3)$ derived from equation (4). It is apparent that

TABLE II.

t.	$\Delta x \, . \, 10^3$.	$\bar{v} \, . \, 10^7$.	$e - \frac{1}{2}\Delta x$.	$x \, . \, 10^3$.	$[H^+] \, . \, 10^3$.	$k \, . \, 10^3$.	
			0·0002N-HCl.				
1230	0·348	2·83	0·206	0·174	0·212	6·48	
1431	0·392	2·74	0·206	0·196	0·213	6·24	
2543	0·764	3·00	0·206	0·382	0·225	6·48	
3078	0·964	3·13	0·206	0·482	0·231	6·58	
4213	1·332	3·16	0·205	0·666	0·241	6·40	
6798	2·39	3·51	0·205	1·195	0·267	6·42	
			0·0005N-HCl.				
1523	1·05	6·89	0·206	0·525	0·516	6·49	
2802	1·96	7·00	0·205	0·980	0·529	6·45	
4170	3·01	7·22	0·205	1·50	0·543	6·49	
5711	4·22	7·39	0·204	2·11	0·559	6·48	
5864	4·33	7·38	0·204	2·16	0·560	6·46	
8576	6·54	7·63	0·203	3·27	0·587	6·40	
2905	2·52	8·63	0·205	6·26	0·650	6·51	*
5703	5·01	8·78	0·204	7·50	0·674	6·39	*
2859	2·79	9·76	0·205	11·40	0·741	6·42	†
5709	5·70	9·98	0·203	12·85	0·763	6·45	†
8572	8·62	10·06	0·202	14·3	0·785	6·34	†
			0·001N-HCl.				
2725	3·71	13·62	0·204	1·85	1·027	6·50	
2987	4·08	13·66	0·204	2·04	1·030	6·51	
3970	5·46	13·75	0·203	2·73	1·040	6·51	
5744	8·06	14·03	0·202	4·03	1·059	6·56	
6988	9·84	14·07	0·201	4·92	1·072	6·52	
8630	12·20	14·12	0·200	6·10	1·088	6·50	
			0·002N-HCl.				
1422	3·81	26·8	0·204	1·90	2·015	6·52	
1560	4·16	26·7	0·204	2·08	2·015	6·47	

* In these experiments acetic acid was added at the commencement to give a 0·005N-solution.

† Initial addition of acetic acid to give a 0·01N-solution.

the measured reaction velocities can be satisfactorily interpreted in terms of equation (4), for the variations in the tabulated values of k are within the limits which are attributable to experimental error.

With reference to the magnitude of the autocatalytic effects which are involved, it may be noted that the observed velocity increases by about 25% in the experiments with 0·0002N-hydrochloric acid, and by about 40% in those with 0·0005N-hydrochloric acid. The maximum velocity ($\bar{v} = 10{\cdot}06 \times 10^{-7}$) in the latter series corresponds with a solution in which the mean concentration of the acetic acid is nearly thirty times as great as the concentration of the hydrochloric acid. These figures serve to indicate the range of the variations which are associated with the measurements recorded in the table.

The results afford additional support for the contention that the rate of hydrolysis of ethyl acetate is determined by the hydrogen-ion concentration of the solutions. Considered in the light of Brönsted's "intermediate complex" theory, they would seem to indicate that the primary stage of the reaction consists in the interaction of the hydrogen ion with the electrically neutral ethyl acetate molecule.

Summary.

The catalytic effects produced by hydrochloric acid in the hydrolysis of ethyl acetate have been examined over a wide range of acid concentrations.

A method for the elimination of autocatalytic effects and for the determination of initial velocities is described.

For concentrations of hydrochloric acid between 0·0002 and 0·2 mol. per litre, the initial velocity is proportional to the concentration of the acid.

At all stages the velocity is determined by the hydrogen-ion concentration of the solution.

The catalytic activity of the hydrogen ion would thus appear to be determined by its concentration and not by its thermodynamic activity.

THE UNIVERSITY, LEEDS. [*Received, May 19th, 1928.*]

CCLXXXIII.—*Acid and Salt Effects in Catalysed Reactions. Part XVI. Catalytic Effects in the Iodination of Mesityl Oxide.*

By HARRY MEDFORTH DAWSON and ARTHUR KEY.

THE experiments now to be described originated in the observation that an old sample of acetone sodium bisulphite reacted abnormally quickly with iodine. It was suspected that the presence of con-

densation products might be the cause of this enhanced reactivity, and preliminary experiments with mesityl oxide showed that this substance in dilute aqueous solution reacts very rapidly with iodine and that the change is similar to that which occurs with acetone—the reaction is catalysed by acids, and for a given hydrogen-ion concentration the velocity is proportional to the concentration of the mesityl oxide and independent of the concentration of the iodine. It follows that the rate of disappearance of the iodine is determined by a preliminary change in the mesityl oxide, and that the iodine reacts immediately with the product of this transformation.

For the same concentration of ketone, and with dilute hydrochloric acid (*e.g.*, $0{\cdot}01N$) as catalyst, the mesityl oxide reaction takes place more than 200 times as rapidly as the acetone reaction, and this high speed suggested that a study of the autocatalytic change would provide a convenient starting point in the investigation of the factors which determine the velocity of the reaction.

Early experiments of this kind showed that the course of the autocatalysed reaction is similar to the corresponding reaction with acetone. In its later stages, the velocity can be represented fairly satisfactorily by the simple autocatalytic equation $dx/dt = kmx$, in which m represents the concentration of the mesityl oxide, and x the concentration of the catalytically active hydrogen ion in the form of hydriodic acid, which is measured by the fall in the concentration of the iodine in accordance with the equation $C_6H_{10}O + I_2 \longrightarrow C_6H_9IO + HI$. Integration of the differential equation gives $\log x = kmt +$ constant, and in agreement with this it was found that the plot of $\log x$ against t for the later stages of the reaction gave approximately a straight line. Very considerable deviations from the straight line were always found, however, in the initial period, and these deviations were such as to show clearly that the velocity of the reaction in its early stages is much greater than can be accounted for by the above equation. We were at first inclined to seek an interpretation of these oft-repeated observations in the joint catalytic action of the hydrogen and hydroxyl ions, but later experiments showed quite definitely that the combined action of these ions does not account for the facts, which, indeed, can only be explained by the further assumption that catalytic effects of considerable magnitude are to be attributed to the undissociated water molecules.

Attention may first be directed to some of the difficulties which were encountered in the earlier experiments on the autocatalysed reaction. These showed large differences in the behaviour in the initial stages of the reaction when different samples of mesityl

oxide were employed. Some of the latter were obtained by repeated fractional distillation of commercial specimens, and others were prepared by us from acetone by conversion into diacetone-alcohol which was separated and subsequently converted into mesityl oxide by distillation with a very small quantity of iodine (Hibbert, *J. Amer. Chem. Soc.*, 1915, **37**, 1748). With such samples of mesityl oxide, which were almost identical in density and refractive index, the times required for the autocatalysed change to proceed to the same point under precisely the same conditions varied very widely. With a concentration of 4 c.c. of mesityl oxide and 0·001 mol. of iodine per litre, the time occupied by the disappearance of the iodine ranged from 40 to 200 minutes, although the course of the reaction in the later stages was the same in each case within narrow limits.

These results directed our attention to observations recorded by Harries (*Ber.*, 1899, **32**, 1329; *Annalen*, 1904, **330**, 189), who found that a specimen of mesityl oxide could not be entirely dissolved in a 40% solution of sodium bisulphite. The insoluble fraction, amounting to 30%, differed but little in density and refractive index from the original and gave the same *cis*- and *trans*-oximes. Since the mesityl oxide recovered from the bisulphite solution dissolved completely on renewed treatment with this reagent, Harries came to the conclusion that mesityl oxide is not chemically homogeneous and that a new type of isomerism is involved. In similar experiments, Morton (*J.*, 1926, 719) failed to detect any such abnormality in the behaviour of mesityl oxide, and inferred that some unrecorded factor was involved in the work of Harries. Our own observations would suggest that the mesityl oxide examined by the latter was impure, for we have found that the miscibility of mesityl oxide with water is very greatly reduced by the impurities which are usually present in the ordinary preparations.

In partial explanation of the inconsistencies in the behaviour of different samples of mesityl oxide in the autocatalysed reaction with iodine, it was found that these contained varying amounts of an acidic substance which is not removed by distillation, but which can be separated by treatment with a dilute solution of alkali, or even by repeated extraction with water. After such treatment, the various samples showed much closer agreement in their behaviour under the conditions afforded by autocatalysis. When, however, these acid-free specimens were examined with reference to the velocity of iodination in acetate buffers of p_H 5—5·5, they exhibited marked differences, and this suggested the presence of a non-acid impurity. The removal of this was eventually effected by crystallising the mesityl oxide from a solution of the acid-free samples in

light petroleum. By the use of liquid air to obtain the necessary low temperature, the crystals were separated by filtration and freed from solvent by distillation. The mesityl oxide was then examined by measuring the velocity of iodination in an acetate buffer of p_H 5·2. The results obtained after one, two, and three crystallisations were :

Mesityl oxide (acid-free).	M. p.	Velocity of iodination.
Purified by distillation	−44·0°	2·0
Once crystallised	−42·5	1·2
Twice crystallised	−41·5	0·91
Thrice crystallised	−41·5	0·87

From the above data it would appear that the product obtained in the second crystallisation is very nearly pure, and this is the material which has been used in our final experiments. These, it may be noted, have not disclosed any factor which was not already indicated in the earlier experiments with less pure samples of mesityl oxide.

Under the conditions of the experiments which we have made with mesityl oxide, there is a close similarity in the behaviour of this substance and of acetone towards iodine, but it should be noted that marked differences are shown in the reactivity of the respective iodo-substitution products. The iodomesityl oxide would appear to undergo hydrolysis very readily, for when the solution in which the reaction has proceeded to completion is titrated with standard alkali and phenolphthalein as indicator, the consumption of alkali is nearly twice that required by the hydriodic acid formed in the primary reaction. The iodomesityl oxide also reacts readily with sodium thiosulphate, and the reactivity disclosed by these observations restricts to some extent the range of the conditions which are suitable for measurements of the velocity of iodination. There are, however, substantial grounds for the belief that the essential factors associated with this reaction have been identified and evaluated. The measurements to be described include observations on the catalytic activity of hydrochloric and acetic acids, on the velocity in buffer solutions, and on the course of the autocatalysed reaction. On account of the limited solubility of (impure) mesityl oxide in water, the solvent used at first contained 5% (vol.) of alcohol, and since this solvent facilitated the addition of small quantities of mesityl oxide in the form of an alcoholic solution, it was employed in all the experiments. The standard concentration of the mesityl oxide was 4·00 c.c. per litre (0·035*M*), and as a rule iodine was added to give a 0·001*M*-solution. The temperature was 25°.

Hydrochloric Acid as Catalyst.—In consequence of the high speed

of the reaction in dilute hydrochloric acid solution, the progress of the change could not be followed by the customary method of titration with standard thiosulphate, and the following method was therefore adopted. At a given instant the reaction was started by the addition of a measured quantity of iodine to the solution containing the mesityl oxide and hydrochloric acid, and when the reaction was nearly completed a little starch paste was added and the time noted at which the blue colour disappeared. This method has also been used in some of the experiments with acetic acid as catalyst. Such experiments give the mean reaction velocity $\bar{v}$, and from a series in which the quantity of added iodine is varied, it is possible to determine the initial velocity of the reaction. Table I gives the results for such experiments with $0{\cdot}0101N$-hydrochloric and with $0{\cdot}05N$-acetic acid.

TABLE I.

$0{\cdot}0101N$-HCl.			$0{\cdot}05N$-$CH_3{\cdot}CO_2H$.		
I_2 (mol./l.).	t (mins.).	$\bar{v} \times 10^4$.	I_2 (mol./l.).	t (mins.).	$\bar{v} \times 10^4$.
0·0005	3·20	1·56	0·0005	30·9	0·162
0·0010	6·27	1·60	0·0010	54·5	0·183
0·0015	9·16	1·64	0·0015	72·8	0·206

In each series, the mean velocity increases with the iodine concentration. This is connected with the increasing catalytic effect of the hydriodic acid produced, although the influence of the latter is to some extent counteracted by a fall in the concentration of the mesityl oxide. It is sufficient to note that the mean velocity is a linear function of the original iodine concentration and therefore that it is possible to derive the initial velocities for each series. The values so obtained are $1{\cdot}52 \times 10^{-4}$ for $0{\cdot}0101N$-hydrochloric acid and $0{\cdot}141 \times 10^{-4}$ for $0{\cdot}05N$-acetic acid.

From similar series of experiments with hydrochloric acid solutions of varying concentration, it has been found that the initial velocity (v_0) is almost exactly proportional to the concentration (c). On the assumption that the catalytic effect under these conditions is attributable to the hydrogen ion, these experiments give for $k_h = v_0/c$ the value 0·015. Other observations suggest a somewhat lower value, *viz.*, $k_h = 0{\cdot}0147$.

Reaction Velocity in Buffer Solutions.—The possibility that the unexpectedly high speed which had been observed in the early stages of the autocatalysed reaction might be due to the catalytic effect of water molecules led us to investigate the velocity of the reaction in buffer solutions of different p_H and various concentrations. For a buffer solution containing the weak acid HA and the salt MA, the observed reaction velocity may be represented by

$$v = v_h + v_{OH} + v_w + v_a + v_m \quad . \quad . \quad . \quad . \quad (1)$$

in which the successive partial velocities correspond with the catalytic action of the hydrogen ion, the hydroxyl ion, the water molecule, the acid ion A^-, and the undissociated acid molecule HA. When the acid–salt ratio of the buffer mixture has a fixed value, the first three partial velocities are constant and the above equation may be written

$$v = v_0 + v_b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

where v_0, which represents the velocity at zero buffer concentration, depends only on the hydrogen-ion concentration, and v_b, which represents the catalytic effect of the buffer constituents, is proportional to the concentration of the buffer solution. In other words, the measured velocity v is a linear function of the concentration of the buffer. Velocity measurements for a fixed buffer ratio and varying buffer concentration lead, therefore, by linear extrapolation to the corresponding v_0, and such v_0 values in their dependence on p_H correspond with points on the water catenary (H^+–H_2O–OH^-).

Acetate buffers were used for the most part, but the higher p_H values were stabilised by means of phosphate buffers. Since the solvent contains 5% of alcohol, the dissociation constants of the acetic and phosphoric acids are appreciably less than for pure water. In the case of acetic acid this reduction is indicated by measurements of conductivity and of hydrogen potential, and comparative observations on the catalytic activity of acetic acid in water and in 5% alcohol suggest that the constant is reduced from $1{\cdot}85 \times 10^{-5}$ to $1{\cdot}7 \times 10^{-5}$. It will be assumed that the proportional reduction in the second-stage constant K_2 for phosphoric acid has the same value, *i.e.*, if $K_2 = 1{\cdot}1 \times 10^{-7}$ for aqueous solution, the value for 5% alcoholic solution becomes $1{\cdot}0 \times 10^{-7}$.

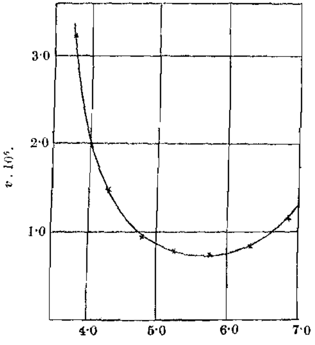
In Table II the results are summarised. The buffer mixtures are indicated in col. 1; col. 2 gives the p_H; col. 3 the hydrogen-ion concentrations derived from the ionisation constants of the acids; col. 4 the concentrations of the acid (c') and salt (s); col. 5 the observed initial velocities; and col. 6 the values of v_0 derived by extrapolation from the straight line which gives the connexion between v and c' (or s).

When the values of v_0 are plotted against p_H the catenary curve shown in Fig. 1 is obtained. According to this the minimum velocity v_i is $0{\cdot}75 \times 10^{-6}$, and the p_H of the isocatalytic point 5·68 or $[H^+]_i = 2{\cdot}1 \times 10^{-6}$. This minimum velocity is about twelve times the magnitude of the velocity due to the joint action of the hydrogen and hydroxyl ions, for the latter is given by $u_i = 2k_h[H^+]_i = 2 \times 0{\cdot}0147 \times 2{\cdot}1 \times 10^{-6} = 0{\cdot}062 \times 10^{-6}$. The difference between v_i and u_i must be due to the catalytic action of the

TABLE II.

Buffer mixture.	p_H.	$[H^+] . 10^5$.	Buffer concentration, c'.	s.	$v . 10^6$.	$v_0 . 10^6$.
			0·05	0·005	3·42	
10HAc + 1NaAc	3·77	17·0	0·1	0·01	3·65	3·22
			0·15	0·015	3·84	
			0·015	0·005	1·55	
3HAc + 1NaAc	4·29	5·1	0·03	0·01	1·64	1·46
			0·045	0·015	1·74	
			0·005	0·005	1·00	
1HAc + 1NaAc	4·77	1·7	0·01	0·01	1·05	0·94
			0·015	0·015	1·12	
			0·005	0·015	0·91	
1HAc + 3NaAc	5·24	0·57	0·01	0·03	1·03	0·79
			0·015	0·045	1·14	
			0·002	0·02	0·89	
1HAc + 10NaAc	5·77	0·17	0·004	0·04	1·04	0·75
			0·006	0·06	1·18	
			$c' + s =$ 0·01		0·90	
$4·81NaH_2PO_4$ + $1Na_2HPO_4$	6·32	0·048	= 0·02		0·97	0·82
			= 0·03		1·06	
			$c' + s =$ 0·01		1·29	
$1·41NaH_2PO_4$ + $1Na_2HPO_4$	6·85	0·014	= 0·02		1·43	1·15
			= 0·03		1·56	

FIG. 1.



The water catenary (v_0–p_H) for the mesityl oxide–iodine reaction.

water molecules; in other words, $v_w = 0·69 \times 10^{-6}$. Furthermore if $K_w = 10^{-14}$, we derive from $[H^+]_i = k_{OH}K_w/k_h$ the value $k_{OH} = 6·$ for the catalytic coefficient which characterises the hydroxyl ion From $k_h = 0·0147$, $k_{OH} = 6·5$, and $v_w = 0·69 \times 10^{-6}$, the reactio

velocities corresponding with the water catenary may now be calculated by use of the equation

$$v_0 = 0{\cdot}0147[H^+] + 6{\cdot}5[OH^-] + 0{\cdot}69 \times 10^{-6}$$

and in Table III these are compared with the velocities derived from the buffer solution experiments. Col. 2 shows the hydrogen-ion concentration; cols. 3, 4, and 5 the partial velocities v_h, v_{OH}, and v_w, respectively; col. 6 the calculated velocity v_o; and col. 7 the observed velocity.

TABLE III.

Buffer.	$[H^+] . 10^5$.	$v_h . 10^6$.	$v_{OH} . 10^6$.	$v_w . 10^6$.	$v_0 . 10^6$. (calc.).	$v_0 . 10^6$. (obs.).
10HAc + 1NaAc	17·0	2·50	—	0·69	3·19	3·22
3HAc + 1NaAc	5·1	0·75	—	0·69	1·44	1·46
1HAc + 1NaAc	1·7	0·25	—	0·69	0·94	0·94
1HAc + 3NaAc	0·57	0·084	0·01	0·69	0·785	0·79
1HAc + 10NaAc	0·17	0·025	0·04	0·69	0·755	0·75
$4{\cdot}81NaH_2PO_4$ + $1Na_2HPO_4$	0·048	0·01	0·135	0·69	0·835	0·82
$1{\cdot}41NaH_2PO_4$ + $1Na_2HPO_4$	0·014	—	0·465	0·69	1·155	1·15

From the reaction-velocity data for the buffer solutions, it is possible to derive the values of k_m and k_a for the buffer constituents HA and A^-. If $q = c'/s$ is the ratio of acid to salt in the buffer mixture, the equation for the velocity may be written

$$v = v_0 + (k_a + k_m q)s$$
$$= v_0 + ls$$

where $l = k_a + k_m q$ is the slope of the curve which is obtained when the velocity for a given buffer ratio is plotted against the buffer concentration of the salt. If q' and l' are corresponding values for a second series of buffers, we obtain

$$k_m = (l - l')/(q - q') \quad . \; . \; . \; (2) \qquad k_a = (ql' - q'l)/(q - q') \quad . \; . \; . \; (3)$$

The values derived in this way are $k_m = 3{\cdot}5 \times 10^{-6}$ for the acetic acid molecule, $k_a = 7 \times 10^{-6}$ for the acetic ion, $k = 3 \times 10^{-6}$ for the H_2PO_4' ion, and $k = 30 \times 10^{-6}$ for the HPO_4'' ion. The much greater activity of the HPO_4'' ion compared with the H_2PO_4' ion is consistent with the general relation that the activity of the anion increases as the ionisation constant of the corresponding acid diminishes.

Acetic Acid as Catalyst.—Under the conditions of these experiments, the reaction velocity is determined by the joint action of the hydrogen ion, the acetic acid molecule, and the water molecule, for the general equation may be written

$$v = (k_h + k_a - k_m)[H^+] + k_m c_1 + v_w \quad . \; . \; . \; (1b)$$
$$= 0{\cdot}0147\,[H^+] + 3{\cdot}5 \times 10^{-6} c_1 + 0{\cdot}69 \times 10^{-6}$$

where c_1 is the concentration of the acetic acid. The velocity may be measured by titration of the residual iodine with thiosulphate or by the colour-disappearance method used in the case of hydrochloric acid. Both methods have been applied with concordant results.

In Table IV, col. 1 gives the method of observation, col. 2 the concentration of the acetic acid, col. 3 the hydrogen-ion concentration calculated from $K = 1{\cdot}7 \times 10^{-5}$, col. 4 the velocity calculated from equation (1*b*), and col. 5 the observed initial velocity. It is apparent that the observations made with acetic acid are satisfactorily interpreted in terms of (1*b*).

TABLE IV.

Method.	c_1.	$[H^+] . 10^3$.	$v . 10^6$ (calc.).	$v . 10^6$ (obs.).
Titration	0·02	0·58	9·3	9·2
Colour	0·05	0·92	14·4	14·1
Colour	0·1	1·30	20·1	20·0
Titration	0·1	1·30	20·1	20·2
Colour	0·2	1·84	28·4	27·7

The Autocatalysed Reaction.—When the mesityl oxide and iodine are dissolved in "conductivity" water, the only catalysts would appear to be the hydrogen ion, the hydroxyl ion, and the water molecule. When the reaction has proceeded far enough to permit of a measurement of the fall in the iodine concentration, the hydrogen-ion concentration of the solution is controlled by the hydriodic acid formed, and the equation for the velocity may be written

$$v = dx/dt = k_h x + k_{OH} K_w / x + v_w \quad . \quad . \quad . \quad (4)$$

If the numerical values of k_h, k_{OH}, K_w, and v_w are introduced in this equation, it is at once apparent that the partial velocity due to the hydroxyl ion may be entirely neglected when the reaction has reached the stage of measurable x values. The equation then becomes

$$dx/dt = k_h x + v_w \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

which by integration yields

$$k_h t = 2{\cdot}30 \log_{10}(x + v_w/k_h) + \text{constant} \quad . \quad . \quad . \quad (4b)$$

Since $v_w/k_h = 0{\cdot}000047$, it follows that $\log(x + 0{\cdot}000047)$ should be a linear function of t.

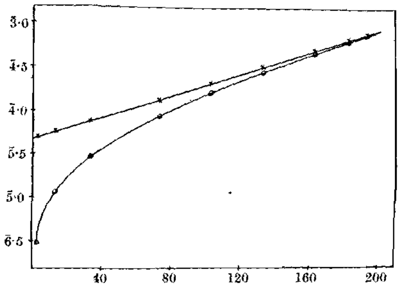
In the determination of x, the samples to be titrated were run into a dilute acetate buffer p_H 5·7, which corresponds with the minimum velocity on the water catenary. The experimental data for such an experiment under autocatalytic conditions were:

t (mins.)	3	13	33	73	103	133	163	183	193
$x . 10^4$	0·030	0·115	0·30	0·875	1·585	2·71	4·41	6·03	7·04

The graphs of log $(x + 0{\cdot}000047)$ and of log x against t are shown in Fig. 2. If the reaction velocity were entirely controlled by the hydrogen-ion concentration, the latter should be a straight line. The fact that the slope of the curve increases as we approach the beginning of the reaction is a clear indication of the intervention of *some other catalytic* effect, whilst the linearity of the first graph would seem to show that this catalytic effect is represented by the action of the water molecules.

Since this line intersects the ordinate for $t = 0$ at $\bar{5}{\cdot}67$, which is $\log_{10} 0{\cdot}000047$, it follows that $x = 0$ when $t = 0$. Interpreted in

Fig. 2.



Autocatalysis of the mesityl oxide–iodine reaction. Plots of log $(x + 0{\cdot}000047)$ *(curve* $\times$*) and of log* x *(curve* ⊙*) against time.*

the light of the relations shown by the autocatalysed reaction between acetone and iodine (Dawson, J., 1927, 458), the conclusion to be drawn from this is that the catalytic action of the hydroxyl ion, as represented by the second term in (4), has no appreciable influence on the course of the autocatalysed mesityl oxide reaction. This accords with the relatively low value of $k_{OH}/k_h = 440$ for this reaction, whereas the corresponding ratio for the acetone reaction is 15,000. In the former case the hydrogen-ion concentration of the minimum velocity (*M.V.*) point is $2{\cdot}1 \times 10^{-6}$, whilst for the acetone reaction it is $12{\cdot}5 \times 10^{-6}$ (compare Dawson and Key, this vol., p. 543).

Although, therefore, there can be no doubt that the reaction velocity, as represented by (4), passes through a minimum value, the incidence of this corresponds with a value of x which is far too

small for quantitative measurement. The $M.V.$ point would appear to be reached in about 2 minutes, and because of the large catalytic effect of the water molecules ($v_w = 0{\cdot}69 \times 10^{-6}$) as compared with that due to the hydrogen and hydroxyl ions ($v_h + v_{OH} = 0{\cdot}06 \times 10^{-6}$), the incidence of minimum velocity has very little influence on the course of the autocatalysed reaction.

In the derivation of (4*b*) it was assumed that the concentration of the mesityl oxide remains constant throughout the autocatalysed reaction. When this is not the case, the equation for the velocity becomes

$$dx/dt = k_h x(1 - x/m) + v_w(1 - x/m) \quad . \quad . \quad (5a)$$

which on integration becomes

$$k_h t = 2{\cdot}30/(1 + v_w/k_h m) . \log_{10}(x + v_w/k_h)/(1 - x/m) + \text{constant} \quad (5b)$$

where m is the molar concentration of the mesityl oxide.

In the experiment shown in Fig. 2, the total fall in the concentration of the mesityl oxide amounts to 2%, and when equation (4*b*) is applied to the interval between $t = 163$ and $t = 193$ minutes, at which stage of the reaction the effect of the water molecules is small compared with that due to the hydrogen ion, we obtain $k_h = 0{\cdot}01435$, and this, when corrected for the fall in the mesityl oxide concentration below the standard value of 0·035 mol. per litre, gives $k_h = 0{\cdot}0146$, in close agreement with the figure previously given.

Comparison of the Coefficients for the Acetone and Mesityl Oxide Reactions.—As a matter of practical convenience, the velocity coefficients which have been derived from the experiments with acetone and mesityl oxide are in both cases expressed in terms of the respective concentrations of these substances which were actually used in the observations. The concentration of the acetone was 0·272 molar (20·0 c.c. per litre), and that of the mesityl oxide 0·035 molar (4·00 c.c. per litre). In the comparison instituted in Table V, the two series of coefficients are referred to molar concentration of the ketone. The last column shows the ratios of the corresponding coefficients.

TABLE V.

Catalytic coefficient.	Acetone reaction.	Mesityl oxide reaction.	Ratio.
k_h	$1{\cdot}72 \times 10^{-3}$	420×10^{-3}	·233
k_{OH}	25	185	7·5
$k_w = v_w/55$	5×10^{-10}	3700×10^{-10}	750
k_m ($CH_3{\cdot}CO_2H$)	$5{\cdot}5 \times 10^{-6}$	100×10^{-6}	18
k_a ($CH_3{\cdot}CO_2^-$)	15×10^{-6}	200×10^{-6}	13

In considering these ratios, it should be noted that the value for k_h can be determined much more precisely than the values for the

ther catalytic entities. Indirect methods have to be used in the erivation of the value for k_{OH}, and in the case of k_w the activity of he water molecule in the acetone reaction is so very small that the egree of precision is limited. It is, however, quite clear that the atio varies widely with the nature of the catalysing entity. In the ase of the hydroxyl ion, the acetic ion, and the acetic acid molecule, he change in the magnitude of the catalytic coefficient on passing om the acetone to the mesityl oxide reaction is of the same order; or the hydrogen ion and for the water molecule the change is uch greater. It does not seem possible to explain these differences.

Summary.

The reaction between mesityl oxide and iodine in dilute aqueous olution is similar to, but more rapid than, the reaction between cetone and iodine.

The iodine takes no part in the primary change, but the rate at hich it disappears affords a measure of the transformation of the esityl oxide, which is probably of the keto-enol type. The eaction is catalysed by hydrogen ions, hydroxyl ions, and water olecules, and also by other acid molecules and the corresponding nions.

The catalytic coefficients for H^+, OH^-, H_2O, $CH_3{\cdot}CO_2H$, $CH_3{\cdot}CO_2^-$, $[_2PO_4^-$, and $HPO_4^=$ have been determined. The relative values of ese coefficients for the mesityl oxide reaction differ very conderably from their relative values for the acetone reaction.

The course of the autocatalysed reaction can be explained in terms f the joint catalytic action of the hydrogen ion and the water olecule.

Mesityl oxide has been prepared in pure condition, and anomalies corded in the literature of this substance are ascribed to the presence f impurities.

The authors desire to acknowledge the assistance rendered in e preliminary stages of this work by Mr. L. H. Angus, Mr. G. laxton, and Dr. C. R. Hoskins. One of us (A. K.) is indebted to e Department of Scientific and Industrial Research for a grant hich has enabled him to take part in this work.

THE UNIVERSITY, LEEDS. [*Received, June 1st, 1928.*]

CCLXXXIV.—*Hydrolysis in Solutions of Potassium Laurate as measured by Extraction with Benzene.*

By JAMES WILLIAM McBAIN and MONROE EATON.

THE hydrolysis of soap solutions is a property only of the simple fatty ions, and its extent is largely due to the almost quantitative disappearance of free fatty acid to form acid soap. Thus all soap solutions are alkaline, far more so than would be expected from the dissociation constants of the fatty acids,* and concentrated soap solutions are less alkaline than dilute ones. Likewise, contrary to a still almost universal preconception, soap solutions are always unsaturated with regard to fatty acid, in spite of the low solubility of the fatty acid (McBain, Taylor, and Laing, J., 1922, **121**, 621; McBain and Buckingham, J., 1927, 2679, which see for further references).

The present communication develops the methods employed by McBain and Buckingham (*loc. cit.*) with sodium palmitate, applying them to various solutions of potassium laurate with and without other additions at 25°. Reference should be made to the previous paper for a discussion of many of the points at issue and the general nature of the results previously obtained.

EXPERIMENTAL.

The work to be described consists of experiments on the composition of a wide range of solutions of potassium laurate with and without additions of alkali or lauric acid. Additional experiments are described which were designed (1) to show that complete reversible equilibrium is attained,† (2) to find the concentration of lauric acid in benzene that is in equilibrium with unaltered aqueous potassium laurate solutions, (3) to measure the solubility of the various constitnents in benzene singly and together, (4) to measure the alkalinity by hydrogen electrode and by indicator, and finally (5) to study the effect of potassium chloride and of carbon dioxide upon the alkalinity and extractability of the aqueous potassium laurate. A few results with aqueous sodium laurate are given for comparison, and some experiments have been carried out with acid

* The dissociation constants are known for the saturated fatty acids up to decoic acid, and hence for the next member with an even number of carbon atoms, lauric acid, the dissociation constant must be 1×10^{-5}, which is not so very weak (S. Smiles and P. O. Herzog, "Chemische Konstitution und Physikalische Eigenschafte," p. 526; E. Franke, *Z. physikal. Chem.*, 1895, **16**, 477).

† This was demonstrated for the first time in the experiments of McBain and Buckingham (*loc. cit.*).

potassium laurate, and also with carbon tetrachloride instead of benzene as extracting solvent.

The chief experiments are the determinations of the compositions of aqueous and benzene layers in equilibrium with each other. For the complete interpretation of the data several subsidiary items of information are required. For example, it is found that the approximate solubility of potassium laurate at 25° is 70 g. per 100 g. of water and 0·005 g. per 100 g. of benzene, showing that for the purposes of most of the experiments the soap itself is insoluble in benzene. However, in the section dealing with acid soap it will be shown that when the benzene contains a large proportion of lauric acid the soap is highly soluble in it, forming acid soap. The potassium laurate used was specially made by Kahlbaum but contained 0·5 equiv. % excess of alkali, whereas the sodium laurate contained 1·8 equiv. % excess of lauric acid. They were dried to constant weight at 110°. Kahlbaum's lauric acid was used, and its solubility in 100 g. of benzene at 25° was 186 g.; at 40° there is miscibility in all proportions. The solubility in water at 25° is 0·00017 g. of undissociated lauric acid per 100 g. of water, as determined by conductivity (see p. 2173).

Since the method of analysis of the non-aqueous layer was to evaporate the solution to dryness and weigh the residue of lauric acid, blank experiments were necessary to show that there was no appreciable loss. It was found that when 10 c.c. of a 1·5% benzene solution of lauric acid were evaporated nearly to dryness during ½ hour and the heating was continued for 4 hours at 80°, the maximum loss by volatilisation was 2% of the total lauric acid originally in the benzene. In the extraction experiments, evaporation was carried only to dryness and the temperature was never allowed to rise above 75°, and in most cases the solutions were far more dilute. Hence the error must have been inappreciable.

The benzene used was dried over calcium chloride or potassium hydroxide and twice distilled. It boiled at 79·5—80·5° and left no residue on evaporation. Boiled-out conductivity water ($\kappa = 2 \times 10^{-6}$ mho) was used throughout. Concentrations are all expressed in weight normality (N_w), *i.e.*, as mols. of solute per 1000 g. of solvent. Kahlbaum's purest potassium chloride was dried at 125° for a day; it was insoluble in benzene.

The soap solutions were brought into equilibrium with the benzene layer in horizontal glass tubes about 3 cm. wide and 20 cm. long, which were rotated on their axis at a speed of 11 revs./min. for 48 hours. Even this very gentle stirring tends to emulsify the layers. Hence the tubes were allowed to stand in a vertical position until at least half the benzene layer had cleared. As much as possible

of the clear layer was then pipetted out, weighed, and evaporated to dryness at 70°. From this and a knowledge of the original composition of the system it was then possible to calculate the concentrations and the amounts of lauric acid which had passed out of or into the aqueous layer. The original system was always made up by weighing the constituents into a tube which was immediately sealed to minimise evaporation of the benzene.

Extraction of Lauric Acid from Aqueous Potassium Laurate by Benzene.

The three-component systems here described consist of three phases, the aqueous phase, the benzene solution of extracted lauric acid, and the sediment of the acid soap in the aqueous layer. However, it is much more interesting to add lauric acid as a fourth component with a view to find the concentration of lauric acid in benzene which is just in equilibrium with unaltered soap solution, a higher concentration giving up lauric acid to the soap solution and a lower concentration partly extracting it. The extractability was shown to be the same after one month as after a few days.

Table I gives the results of the equilibrium experiments with potassium laurate with and without added excess of lauric acid. Table II records for comparison a few experiments on sodium laurate. It is seen that sodium laurate is distinctly more extractable than potassium laurate even when the fact is taken into account that the specimen used contained excess of lauric acid (see p. 2167).

The very definite result from these two tables is that the benzene layer is unsaturated with respect to fatty acid. Since the benzene layer is in true reversible equilibrium with the soap layer, the latter must be equally unsaturated. Even when a very appreciable excess of fatty acid is added to the system so that the aqueous layer contains more equivalents of fatty radical than of potassium or sodium, the benzene layer is still very far from being saturated with respect to fatty acid.

Almost every writer has assumed that there is excess of fatty acid, free in liquid or emulsified form, in ordinary soap solutions. This belief is definitely shown to be false by the results of these quantitative experiments and those of McBain and Buckingham (*loc. cit.*). All the soap solutions are alkaline and unsaturated with regard to free fatty acid. Hence when excess of free fatty acid is added to the soap solution it disappears through combination with the soap to form acid soap. An aqueous solution even of acid soap containing twice as much fatty radical as of sodium or potassium is still appreciably alkaline. Experiments described later show that when the non-aqueous layer is made nearly saturated

ith fatty acid, practically all the soap disappears from the aqueous oap solution.

TABLE I.*

quilibrium experiments in which aqueous solutions of potassium aurate were shaken at 25° with benzene, to which in some cases lauric acid had been added in advance.

Soap soln. (g.).	Benzene (g.).	HL in benzene. Before (g.).	After (g.).	After † (N_w).	N_w of OH′ (aqueous, after).
		$0{\cdot}493N_w$-Potassium laurate.			
15·08	10·31	0	0·00122	0·00059	0·005
15·96	10·30	0	0·00152	0·00073	0·004
		$0{\cdot}25N_w$-Potassium laurate.			
36·81	10·83	0	0·00185	0·00085	0·005
35·42	10·83	0	0·00161	0·00074	0·006
59·61	18·20	0	0·00327	0·00090	0·005
29·33	11·90	0	0·00224	0·00090	0·005
27·38	8·16	0	0·00192	0·00085	0·005
45·02	12·11	0·0031	0·00322	0·00132	0·003
55·46	11·92	0·0076	0·00302	0·00127	0·003
49·37	16·08	0·0242	0·00614	0·00189	0·002
58·30	17·91	0·0406	0·01438	0·00400	0·001
72·00	15·67	0·0753	0·01444	0·00460	0·0009
54·67	17·82	0·1569	0·02884	0·0081	0·0005
		$0{\cdot}1N_w$-Potassium laurate.			
39·78	17·01	0	0·01202	0·0035	0·001
19·27	9·13	0	0·00486	0·0027	0·002
24·64	10·31	0	0·00553	0·0027	0·002
24·75	10·23	0	0·00514	0·0025	0·002
24·69	10·35	0	0·00361	0·0017	0·003
24·66	10·35	0	0·00322	0·0016	0·003
24·73	10·36	0	0·00320	0·0016	0·003
40·02	11·03	0	0·00504	0·0023	0·002
36·87	10·21	0	0·00546	0·0027	0·002
43·02	18·30	0·0031	0·0175	0·0039	0·001
48·23	18·37	0·0110	0·0175	0·0048	0·001
41·01	14·78	0·0057	0·0077	0·0025	0·002
51·43	10·08	0·0066	0·0064	0·0032	0·002
43·83	12·39	0·0186	0·0119	0·0048	0·001
43·90	12·86	0·0230	0·0156	0·0061	0·0009
44·70	12·30	0·0273	0·0210	0·0085	0·0006
43·04	16·96	0·0571	0·0419	0·0123	0·0004
37·63	13·81	0·0782	0·0471	0·0172	0·0003
37·30	13·54	0·1019	0·0646	0·0239	0·0002
40·74	13·58	0·2234	0·1466	0·0545	0·0001
44·00	16·97	0·3424	0·2245	0·0654	0·0001

* In experiments with $1{\cdot}0N_w$-potassium laurate, emulsification was so great that it was only after 2 months' standing that about one-tenth of the benzene layer could be withdrawn for analysis, and the lauric acid in two such samples was too small to be weighable. This is probably due to (*a*) the small concentration of hydrolysable simple laurate ion, and (*b*) the completeness with which any fatty acid formed is combined in this high concentration of soap.

† A saturated solution of lauric acid would have been $9{\cdot}3N_w$.

TABLE I (*continued*).

Soap soln. (g.).	Benzene (g.).	HL in benzene. Before (g.).	After (g.).	After * (N_w).	N_w of OH′ (aqueous, after).
		$0·05N_w$-Potassium laurate.			
26·00	10·31	0	0·00620	0·00299	0·002
26·59	10·33	0	0·00548	0·00250	0·002
26·17	10·33	0	0·00708	0·00341	0·002
34·21	*8·079*	*0*	*0·00576*	*0·00356*	*0·0015*
30·86	8·64	0	0·00508	0·00294	0·001
30·29	7·08	0	0·00455	0·00320	0·001
33·99	9·95	0·0039	0·00723	0·00362	0·001
35·87	8·28	0·0082	0·00855	0·00515	0·001
31·02	6·95	0·0173	0·0148	0·01308	0·0004
30·64	7·26	0·03336	0·02526	0·01737	0·0003
31·10	14·37	0·04703	0·03152	0·01094	0·0005
29·55	8·16	0·06952	0·05672	0·03462	0·00015
30·25	5·97	0·05097	0·03115	0·02595	0·0002
30·47	8·17	0·0997	0·08580	0·0524	0·0001
27·74	*9·67*	*0·1228*	*0·1077*	*0·0556*	*0·0001*
32·10	9·39	0·3884	0·3446	0·1832	0·00003
		$0·01N_w$-Potassium laurate.			
24·68	4·37	0	0·00331	0·00373	0·0003
24·42	12·34	0	0·00456	0·00184	0·0005
24·67	10·32	0	0·00442	0·00214	0·0005
47·92	10·45	0	0·00418	0·00198	0·0006
33·71	12·60	0·0024	0·00819	0·00324	0·0003
48·34	9·55	0·0046	0·01275	0·00667	0·0001
41·32	10·43	0·0094	0·01241	0·00595	0·0002
46·68	*15·68*	*0·0157*	*0·0174*	*0·00555*	*0·0002*
57·80	10·56	0·0251	0·0256	0·0121	0·0001
49·90	13·37	0·1156	0·1156	0·0431	0·00003
48·07	*12·22*	*0·2111*	*0·2036*	*0·0829*	*0·00001*
		$0·005N_w$-Potassium laurate.			
24·70	*4·29*	*0*	*0·00297*	*0·00346*	*0·0001*
25·13	10·33	0	0·00349	0·00168	0·0003
25·32	10·35	0	0·00356	0·00172	0·0003
25·26	10·35	0	0·00418	0·00202	0·0002
		$0·001N_w$-Potassium laurate.			
62·30	12·88	0	0·00224	0·00085	0·0002
60·70	12·89	0	0·00311	0·00120	0·0001
71·09	11·72	0	0·00643	0·0027	0·00004
83·49	14·06	0·0123	0·0228	—	—
103·74	21·43	0·0223	0·0279	0·0063	0·00002
60·28	*13·34*	*0·1895*	*0·1899*	*0·0710*	*0·000002*
117·47	27·35	0·5388	0·5345	0·0968	0·000001
68·75	13·08	0·3085	0·3043	0·1163	0·000001

* A saturated solution of lauric acid would have been $9·3N_w$.

Referring to the data of Tables I and II, it is evident that the amount of fatty acid extracted from an aqueous soap solution increases with the various factors as expected; *i.e.*, the extractability increases with increasing proportion of extracting solvent, with decreasing alkalinity of the soap, with increasing amounts of fatty acid added to the soap solution, or with increasing dilution of the soap, and hence increased proportion of hydrolysable simple fatty ion.

TABLE II.

Equilibrium experiments in which aqueous solutions of sodium laurate were shaken at 25° with benzene.

Soap soln. (g.).	Benzene (g.).	HL in benzene, (g.).	HL in benzene, (N_w).	N_w of OH' (aqueous after).*
		$0{\cdot}10N_w$-Sodium laurate.		
45·91	15·46	0·02141	0·00692	0·0008
51·06	21·07	0·02662	0·00617	0·0008
		$0{\cdot}05N_w$-Sodium laurate.		
45·71	13·39	0·01851	0·00691	0·0008
48·07	21·63	0·02185	0·00503	0·0011
29·52	12·08	0·01380	0·00571	0·0009

* Concentration of L' has not been measured in solutions of NaL at 25°; it is therefore assumed to be the same as that in a KL solution of the same concentration.

With very dilute soap solutions, the effect of carbon dioxide becomes a serious source of error. Although carbon dioxide is a much weaker acid than any of the fatty acids, we find that if it is passed through an $N/100$-soap solution in the process of extraction, the whole of the fatty acid passes into the benzene layer owing to complete neutralisation of the hydroxyl ion in the aqueous layer by the carbonic acid. The results with solutions below $0{\cdot}01N_w$ are increasingly influenced by ingress of carbon dioxide, in spite of precautions taken. In four out of six experiments with $0{\cdot}0005N_w$-potassium laurate, practically all the lauric acid was removed by the benzene. This is to be expected in a solution sufficiently dilute, although a minute trace of free lauric acid must always remain dissolved in the aqueous phase.

In order to evaluate the concentrations of the various constituents in a soap solution in equilibrium with a benzene solution of fatty acid, it is necessary to know the distribution ratio for lauric acid, the dissociation constant of water (K_w), and the dissociation constant of the lauric acid ($K_a = 1 \times 10^{-5}$). The concentration of simple laurate ion in aqueous soap solution is known from previous studies of freezing point and conductivity (McBain and Jenkins, J., 1922, **121**, 2325). Since the concentration of undissociated lauric acid in the aqueous layer is proportional to that in the benzene layer multiplied by the distribution ratio, the equation for hydrolytic equilibrium is:

$$\frac{[\mathrm{L}']}{[\mathrm{OH}'] \times N_w \text{ of lauric acid in } C_6H_6} = K = \frac{K_a}{K_w} \times \text{distribution ratio.}$$

The distribution ratio may be estimated from the results for $0{\cdot}1N_w$-potassium laurate, since this solution was most carefully studied,

and, when neutral (that is, having potassium and laurate stoicheiometrically equivalent to each other), was found to be in equilibrium with the benzene layer, which was $0{\cdot}0055N_w$ with respect to lauric acid. If the hydrolysis alkalinity be taken as $0{\cdot}0009N_w$-OH′, and the concentration of simple laurate ion as $0{\cdot}026N_w$, the distribution ratio would be

$$\frac{0{\cdot}026 \times 10^{-14}}{0{\cdot}0009 \times 0{\cdot}0055 \times 10^{-5}} = 0{\cdot}5 \times 10^{-5},$$

whence the hydrolytic constant $K = 5000$.

This distribution ratio ($0{\cdot}5 \times 10^{-5}$) is that employed in the calculation of the results in Table III, although it is four times larger than the ratio of the solubilities of lauric acid in water and benzene. The discrepancy is not surprising in view of the fact that a saturated solution of lauric acid in benzene is $9{\cdot}3N_w$ and contains almost twice as much lauric acid as benzene. There is a closely similar discrepancy in the distribution ratio of palmitic acid between water and xylene at 90° when saturated solutions are compared with ordinary dilutions.

This approximate distribution ratio enables us to indicate the approximate concentration of free fatty acid in all the soap solutions studied. The most interesting solutions are those whose composition has not been altered, owing to the exactly requisite quantity of lauric acid having previously been added to the benzene layer, so that the two phases are already in equilibrium when first brought together. The results for the series of concentrations of aqueous solutions of potassium laurate containing equivalent quantities of potassium and total fatty radical are contained in Table III.* The concentration of acid soap (N_w) referred to the water, although part of the acid soap is a sediment, is given in the last column of Table III. It is merely the difference in the normality of the OH′ and of the free fatty acid, since if no fatty acid had disappeared to form acid soap, the concentrations of free fatty acid and OH′ must have been identical.

The most striking feature of Table III is that in all pure soap solutions the concentration of free fatty acid is wholly negligible in comparison with the hydrolysis alkalinity. In other words, as

* In calculating the values for N_w of OH′ in Tables I and II, the values for the concentration of laurate ion, L′, as given for unaltered soap solution in Table III are reduced if either lauric acid is extracted from the soap solution by the benzene layer or conversely, forming acid soap. This is allowed for in Tables I and II by multiplying the values for L′ in Table III by the ratio (total laurate radical)/(total potassium), in the aqueous layer, or (total potassium)/(total laurate radical) in the aqueous layer, whichever ratio is less than unity.

TABLE III.

The concentrations of some of the constituents of aqueous potassium laurate solutions at 25°, there being equal equivalents of potassium and laurate radicals in the water, as deduced from the concentration of lauric acid in the benzene layer in equilibrium with the aqueous layer.

Total soap, N_w.	Lauric acid in benzene, N_w.	Laurate ion, N_w.	Lauric acid, $N_w \times 10^{-8}$.	OH′, N_w.	Acid* soap, N_w.
1·0	0·000	0·012	0	—	—
0·25	0·0017	0·021	1	0·002	0·002
0·1	0·0055	0·026	3	0·0009	0·0009
0·05	0·007	0·027	4	0·0008	0·0008
0·01	0·018	0·006	9	0·00007	0·00007
0·001	0·075	0·0009	38	0·0000024	0·000002

* N_w of lauric acid (HL) combined with soap (KL) to form such acid soap as HL,KL.

seen from the practical identity of the last two columns of Table III, the fatty acid set free by hydrolysis goes almost quantitatively to form acid soap.

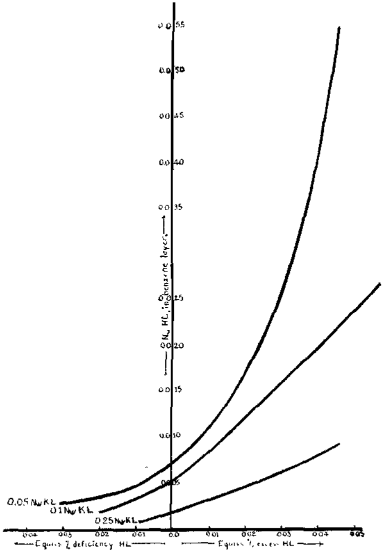
The solubility of lauric acid in water was determined by conductivity and the mode of calculation used by McBain and Taylor (*Z. physikal. Chem.*, 1911, **76**, 179); the specific conductivity of the saturated solution was $4{\cdot}54 \times 10^{-6}$, whence the normality of the undissociated lauric acid in saturated solution in water at 25° is $8{\cdot}8 \times 10^{-6}N_w$.† In pure water, the laurate ion would provide an additional $1 \times 10^{-5}N_w$. This is 300 times greater than the actual concentration of free lauric acid found in a $0{\cdot}1N_w$-solution of potassium laurate, illustrating the utter impossibility of fatty acid in the free liquid or solid state existing in a soap solution. As a check upon the possibility that the solubility of fatty acid in water might be enhanced by such solvents as benzene, the solubility of the lauric acid was similarly determined with water saturated in one case with benzene and in the other with carbon tetrachloride. The specific conductivities were $5{\cdot}23 \times 10^{-6}$ and $4{\cdot}61 \times 10^{-6}$, respectively, whence it is evident that the solubility is not appreciably enhanced. Hence the distribution ratio of lauric acid must be fairly constant for the more dilute soap solutions studied, especially in comparison with the very large changes in the concentration of the benzene layer.

In dilute soap solutions, the percentage of hydrolysis is at a maximum (*e.g.*, it is 9% in $0{\cdot}001N_w$-soap) though the absolute concentration of all constituents is least. In very concentrated

† Lauric acid is therefore much less soluble than silver laurate, although a saturated aqueous solution of lauric acid gives a just noticeable turbidity on addition of excess of silver nitrate.

solution, on the other hand, the crystalloidal constituents including the laurate ion are practically all replaced by colloid except for the sodium or potassium ions also present. The hydrolysis alkalinity therefore passes through a maximum because the colloid serves merely as a reserve from which hydrolysable laurate ion can be

Fig. 1.



The concentration of lauric acid in the benzene layer in equilibrium with solutions of potassium laurate containing deficiency or excess of lauric acid.

formed. However, even the colloidal undissociated soap may play a rôle in the formation of the acid soap. Acid soap itself is a colloidal electrolyte though often of low solubility, hence the extent of its formation does not closely follow the law of mass action. For example, taking a series of benzene solutions of lauric acid sufficiently concentrated for lauric acid to pass from the benzene into the soap

layer, the formation of acid soap does not increase as rapidly as the concentration of the benzene layer.

Fig. 1 of the paper of McBain and Buckingham (*loc. cit.*), which referred to $0{\cdot}1N_w$-sodium palmitate at 90°, shows that fatty acid may be extracted from any soap solution even in the presence of excess of alkali; and likewise that any soap solution is alkaline even when excess of fatty acid has been added. Fig. 1 of the present paper, taken from the results in Table I, shows the similar relations with potassium laurate when excess of alkali or acid is present; *it gives the concentration* of lauric acid in the benzene layer in equilibrium with aqueous soap layer of the composition indicated. The soap solutions on the alkaline side are those from which some of the laurate radical has been extracted by the benzene layer in the form of lauric acid. The designations of the three curves refer to the total concentration of potassium throughout.

Finally, a few experiments may be noted in which it appears that the relative extracting power of benzene and carbon tetrachloride goes parallel with the solubility of lauric acid therein, as expected (Table IV).

TABLE IV.

Solutions of $0{\cdot}05N_w$-potassium laurate.

Soap soln. (g.).	Solvent (g.).	*Lauric acid in solvent.* Before (g.).	After (g.).	After (N_w).*
		Benzene.		
30·86	8·64	0·0	0·00508	0·00294
34·21	8·079	0·0	0·00576	0·00356
		Carbon tetrachloride.		
56·05	24·61	0·0	0·00624	0·00127
32·60	18·73	0·0	0·00389	0·00104

* A saturated solution of lauric acid in benzene would be $9{\cdot}3N_w$, and in carbon tetrachloride $5{\cdot}1N_w$.

Acid Soaps.

As we have seen, pure benzene scarcely dissolves potassium laurate, but it is far otherwise when a large amount of lauric acid is simultaneously present in the benzene. When mixtures of benzene, lauric acid, and potassium laurate are heated together, the whole system becomes homogeneous, and on cooling, crystallisation occurs. In four such experiments the single liquid layer was removed for analysis at 25°, with the following results, potassium laurate being determined as carbonate after ignition:

HL in benzene, N_w	0·042	0·451	3·56	9·28
KL in benzene, N_w	0·0002	0·020	0·065	0·192

The crystals deposited from the above solutions were found by analysis to have the exact composition KL,HL, thus again showing that the solubility of potassium laurate in benzene containing lauric acid is attributable to the formation of acid soap. A crystalline acid soap of this composition was described by Oudemann (*Jahresber.*, 1863, 331) as resulting from warming the potassium laurate and lauric acid in this proportion with aqueous alcohol, but subsequent writers have been unanimous in assuming that acid soap of a definite composition did not occur (see, however, McBain and Stewart's recent description of the definite crystalline acid oleate, KOl,HOl; J., 1927, 1392).

The results given in Table I are not affected by the information just tabulated, since the concentration of lauric acid in the benzene layer was usually well below $0{\cdot}1N_w$. McBain and Buckingham refrained from employing solutions of palmitic acid in xylene exceeding $0{\cdot}25N_w$ in equilibrium experiments with sodium palmitate, because they had observed that with very high concentrations of palmitic acid in xylene the residue on evaporation was greater than the original palmitic acid, and this is now seen to be due to sodium palmitate having entered the xylene layer. They stated that the formation of acid soap was indicated by the soap layer becoming absolutely opaque.

A series of experiments shown in Table V was carried out using a saturated solution of lauric acid in benzene, and the aqueous phase was taken for analysis after filtering off any sediment of acid soap. There was very little emulsification, and most of the acid soap dissolved in the non-aqueous layer. With $0{\cdot}1N_w$-aqueous potassium laurate, both layers were finally almost as clear as water. This is in marked contrast to the experiments reported in Table I, where the aqueous layer became clouded with acid soap when the concentration of lauric acid in the benzene exceeded $0{\cdot}01N_w$.

TABLE V.

Effect of saturated solution of lauric acid in benzene ($9{\cdot}3N_w$) *upon aqueous solutions of potassium laurate at* 25°.

Benzene soln. (g.).	Aqueous soln. (g.).	Aqueous soln. before (N_w).	N_w of total laurate radical left in aqueous layer.
3·701	4·956	0·100	0·0026
4·352	9·444	0·100	0·0051
4·873	6·095	0·250	0·0086
3·591	5·487	0·250	0·0111
8·947	6·442	0·493	0·0039

It is seen from Table V that the soap is almost quantitatively removed from the aqueous solution by contact with a saturated solution of lauric acid in benzene. The aqueous solution must at

last be on the acid side because the lauric acid in the benzene so greatly exceeds the amount of soap in the system. In other words, an aqueous soap solution whose p_H is less than 7 can hardly be prepared. The slight residue of laurate radical in the aqueous layer is probably colloidal acid soap not removed by filtration but materially decreased by increasing the proportion of the benzene layer.

Solid potassium laurate is also capable of largely removing lauric acid from benzene solution, as is shown by the following tabulation of two experiments at 25° in which benzene solutions of lauric acid were used which were too dilute to dissolve much acid soap.

KL, before (g.).	Benzene (g.).	Ratio, total L to total K.	HL, before (g.).	HL left in benzene (g.).	HL removed (%).
3·658	49·37	2·0	3·120	0·423	86·5
0·7336	19·52	1·5	0·3427	0·0048	98·5

Another illustration of the formation of acid soap is given by the action of carbon dioxide upon soap solutions. When a small amount of carbon dioxide is passed over the surface of a soap solution, crystals gradually appear in the upper part of the solution. These crystals are not removed from the solution by extraction with benzene, hence they are not lauric acid. They cannot be potassium laurate, since the solutions are only about 1/30 saturated and the crystals are not dissolved by shaking. We may conclude, therefore, that the first product of the action of carbon dioxide on potassium laurate solutions is acid soap. Soap solutions which have been left exposed to the air for some time show a similar behaviour.

In order to demonstrate the formation of crystalloidal acid soap in aqueous potassium laurate solutions in contact with benzene solutions of lauric acid, an experiment was performed in which the solutions were allowed to stand without shaking. A 0·5N_w-solution of potassium laurate was run into a tube under a saturated solution of lauric acid in benzene. The tube was then sealed and allowed to stand for 2 days. A cake of crystalline acid soap ¼″ thick was formed between the benzene and water layers. From the lower side of the cake, long needles could be seen radiating from various points into the aqueous layer. The crystals were insoluble in water and benzene.

Since potassium laurate is very soluble in water and lauric acid is very soluble in benzene, the formation of a solid solution of potassium laurate in lauric acid under the conditions observed in this experiment is more improbable than the formation of

definite chemical compound. The proof of the existence of definite crystalline acid laurates and palmitates will shortly be published.

Acid soap is a better emulsifying agent than neutral soap, as is evident from the observation made during the experiments of Table I. Miss Laing (*Proc. Roy. Soc.*, 1925, **105**, 28) found that unless the soap solution contains a small excess of alkali the material adsorbed in soap films is acid soap. It may also be mentioned that ready emulsification occurs when a potassium laurate solution, too dilute to contain colloidal soap, is mixed with benzene containing lauric acid.

Effect of Salt upon Extraction and Hydrolysis.

McBain and Buckingham (*loc. cit.*) found that the presence of various salts diminishes the extractibility of aqueous sodium palmitate, in very similar fashion. They pointed out that this was ascribable to repression of the dissociation of the soap into simple laurate ion which is the hydrolysable constituent, and they surmised that the hydrolysis alkalinity was likewise lessened, in accordance with the findings of McBain and Martin (J., 1914, **105**, 957), who used the hydrogen electrode. That a salt greatly decreases the extractability in the case of potassium laurate also is clearly shown in Table VI.

TABLE VI.

Effect of potassium chloride on extractibility of $0{\cdot}1N_w$*-potassium laurate by benzene at* 25°.

Soap soln. (g.).	KCl (N_w).	Benzene (g.).	HL in benzene. Before (g.).	After (g.).	After (N_w).
40·02	0	11·03	0	0·00504	0·00230
49·67	0·0114	10·21	0	0·00215	0·00104
52·41	0·0220	20·28	0	0·00465	0·00112
64·13	0·0499	14·52	0	0·00135	0·00064
35·47	0·2272	5·88	0	0·00079	0·00067

The hydrolysis alkalinity of the final solution in Table VI cannot be calculated, because the concentration of hydrolysable laurate ion is also being diminished. On the other hand, it is possible that formation of acid soap might be facilitated through increase in undissociated potassium laurate and through lowering of the solubility of acid soap by salt, both of which factors act in the direction of increasing the hydrolysis alkalinity. However, it seems probable that the dominant factor is repression of laurate ion with consequent lowering of hydrolysis alkalinity on addition of salt. Direct determinations of the hydrolysis alkalinity are required for a complete answer to this problem.

In Table VII a series of experiments is recorded in which the soap was maintained at $0{\cdot}1N_w$ and the potassium chloride at $0{\cdot}143N_w$; also the weight of soap solution was always 3·5 times that of the benzene, but varying amounts of lauric acid were added.

TABLE VII.

Concentration of lauric acid in the benzene layer at 25° in the five-component system where only the amount of added lauric acid is varied.

HL in benzene, before, g.	0·0021	0·0085	0·0243	0·0708
,, ,, after, g.	0·00301	0·00546	0·00876	0·01117
,, ,, ,, , N_w	0·00161	0·00234	0·00404	0·00517

Comparison of the results given in Table VII with those of Table I or Table III shows that, whereas unaltered $0{\cdot}1N_w$-potassium laurate is in equilibrium with a $0{\cdot}0032N_w$-solution of lauric acid in benzene, the equilibrium concentration in presence of the salt is lowered to $0{\cdot}0023N_w$. In every case salt lowers the extractability, and, for a given addition of lauric acid, increases the amount of acid soap produced in the system.

Summary.

1. The compositions of benzene solutions of lauric acid in equilibrium with various solutions of potassium laurate at 25° have been determined, and the experiments extended to solutions containing various additions.

2. Unaltered soap solutions contain the merest trace of free fatty acid—only a few units per cent. of that capable of dissolving in water. The fatty acid corresponding to the hydrolysis alkalinity is almost quantitatively combined as acid soap.

3. Acid soap forms as a sediment whenever carbon dioxide gains access to the soap solutions. Solid potassium laurate, as well as its aqueous solution, extracts lauric acid from its concentrated solutions in benzene, forming acid soap. The definite crystalline compound, acid potassium laurate, KL,HL, is found to exist, and it is fairly soluble in hot benzene. A concentrated solution of lauric acid in benzene almost quantitatively removes soap. Presence of salts promotes the formation of acid soap but diminishes the extractability of aqueous soap solution.

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CCLXXXV.—*The Rotatory Dispersion of Certain Isomeric Butyl Esters of* l-*Mandelic Acid.*

By Charles Edmund Wood, Albert Edward Chrisman, and Sydney Diggary Nicholas.

The interesting points associated with these esters are that mandelic acid is the simplest hydroxy-acid in the aromatic series and is analogous to lactic acid in the aliphatic series; both *l*-mandelic and *l*-lactic acid are configuratively related to *d*-tartaric acid, but the esters of the first exhibit rotatory dispersion entirely in the negative region, whereas the esters of the second in the homogeneous condition exhibit rotatory dispersion which is situated in general in the positive region (Wood, Such, and Scarf, J., 1923, **123**, 600; 1926, 1928).

Rotatory Power.

The following table indicates that the primary branching of the *n*-butyl chain enhances very considerably the high negative rotation of the *n*-ester; further branching of the chain to the *tert.*-ester brings about a diminution of negative rotation.

Specific rotations $[\alpha]_\lambda^t$ of *l*-mandelates at 45° and 75°.

Ester.	λ 6708.	λ 5893.	λ 5461.	λ 5086.	λ 4359.
			Temp. 45°.		
n-Butyl	−66·3°	−91·1°	−111·0°	−133·6°	−189·0°
*iso*Butyl	73·7	101·9	123·5	148·8	214·3
tert.-Butyl	56·4	78·0	94·5	114·1	162·6
d-*sec.*-Butyl	48·2	67·5	82·0	99·2	151·1
			Temp. 75°.		
n-Butyl	−61·3°	−84·3°	−102·1°	−122·4°	−174·0°
*iso*Butyl	68·0	93·1	113·0	134·8	192·0
tert.-Butyl	52·8	72·9	88·2	106·5	152·8
d-*sec.*-Butyl	44·3	61·5	75·0	90·75	140·1

These results are analogous with respect to the zero axis to those obtained for the alkyl *l*-lactates situated in the positive region, and it appears, therefore, that in both cases the esters, of relative configuration "*d*," formed from a primary *iso*-alcohol have greater rotatory power than the esters of the corresponding normal alcohol, and that further branching of the chain, resulting in the tertiary esters, effects a diminution in rotatory power. The changing alkyl group is contrasted with the strongly negative phenyl group in the mandelates and compared with the positive methyl group in the lactates, and the progressive change of the alkyl grouping leads to a regularity in rotatory effect in the positive and the negative region respectively. The mere comparison of the position of the dispersion curves with respect to the zero axis does not infer a

relative configuration relationship. The types of symmetry (Wood, Such, and Scarf, *loc. cit.*) and of asymmetry produced with the accumulation of identical radicals near the asymmetric carbon atom result in a similar relative position of the dispersion curves of the normal, *iso*-, and *tert.*-esters for "*d*"-mandelic and "*l*"-lactic acids.

d-*sec.*-Butyl *l*-mandelate, containing two centres of optical asymmetry of opposite rotatory power and of the same relative configuration, exhibits a marked decrease in specific rotation which is very pronounced in the violet end of the spectrum. The effect of the active mandelic acid radical, however, dominates the rotatory power, which in all cases is high.

Rotational Displacements in Related Series.

Consideration of Table I shows that (1) the molecular rotatory power is displaced to the right as the normal series of esters is ascended, particularly in passing from the methyl to the ethyl ester; (2) the molecular rotations of the *iso*-esters of lactic, tartaric, glyceric (*iso*butyl), and malic (*iso*butyl) acids are greater than those of the corresponding normal esters, these being situated in the positive region; (3) the molecular rotations of the *iso*-esters of mandelic, α-hydroxybutyric, and glyceric (*iso*propyl) acids exhibit a reverse behaviour, being displaced towards the left; (4) both the tertiary esters of lactic and mandelic acids are displaced towards the zero axis.

The above compounds are of relative configuration "*d*," and although observation (1) may serve in general (Clough, J., 1918, **113**, 526) as a criterion for configuration, no such rule can be applied to the relationship between the *n*-, *iso*-, and *tert.*-esters.

The *n*-esters of tartaric, lactic, hexahydromandelic (Wood and Comley, J., 1924, **125**, 2630), and mandelic acids form an interesting group; for the group, as well as each series, shows a displacement towards the right, the mandelic acid series being situated far down in the negative region, the hexahydromandelic acid series almost on the zero axis, and the tartrates and lactates in the positive region.

In the acetyl and benzoyl derivatives of mandelic acid, acetylation causes a similar displacement of the rotations of both the methyl and the ethyl esters, without change of order, further into the negative region (Freudenberg and Markert, *Ber.*, 1925, **58**, 1753). Similar displacements occur for the diacetyl- and dibenzoyl-*d*-tartrates, as indicated by Table II. (The temperatures 30°, 90°, and 110° have been taken to avoid extrapolation.) When the lactates are considered, however, acetylation causes a *right* displacement without change of order (Freudenberg and Markert, *Ber.*,

TABLE I.

Molecular rotations $[M]_D^t$ of esters.

	CH_3.	C_2H_5.	C_3H_7.	C_4H_9.	C_8H_{17}.	Temp.
l-Mandelic acid.						45°
n-Esters	−255·5 [1]	−210·3 [1]	−191·3 [1]	−189·6		
iso-Esters				−212·1		
tert.-Esters				−162·4		
l-Lactic acid.						20
n-Esters	+8·59	+13·37	+17·44	+19·58	+19·85 [2]	
iso-Esters				+22·16		
tert.-Esters				+13·8		
d-Tartaric acid.						20
n-Esters			+29·34 [3]	+26·75 [4] (21·5°)	+31·87 (45°)	
iso-Esters			+48·91 [3]	+46·50 [3]		
d-Malic acid.						20
n-Esters	+11·10 [5]	+19·34 [5]	+25·33 [5]	+26·37 [6]		
iso-Esters			+22·69 [5]	+27·40 [5]		
d-α-Hydroxy-butyric acid.						15
n-Esters		+2·51 [7]		+15·5 [7]	+11·45 [7] (18°)	
iso-Esters				+12·32 [7]		
l-Glyceric acid.						15
n-Esters	+5·76 [8]	+12·30 [8]	+19·15 [8] (17°)	+21·37 [8] (17°)	+22·28 [8] (19°)	
iso-Esters			+17·5 [8]	+23·05 [8] (18—19·5°)		

[1] Deduced from values obtained by Walker, *J. Physical Chem.*, 1909, **13**, 574

[2] Nonyl ester.

[3] Patterson, J., 1913, **103**, 145.

[4] Frankland and Garner, J., 1919, **115**, 636.

[5] Walden, *Z. physikal. Chem.*, 1895, **17**, 248.

[6] Anschütz and Reitter, *ibid.*, 1895, **16**, 493.

[7] Guye, *Bull. Soc. chim.*, 1896, **15**, 477.

[8] Frankland and MacGregor, J., 1893, **63**, 1415.

TABLE II.

	Temp.	$[M]_\lambda^t$. 6708.	5893.	4678.	Type of dispersion
Methyl tartrate	20°	+ 4·47°	+ 3·67°	− 6·74°	Anom
Ethyl ,, ...	20	+14·50	+16·14	+11·54	,,
Methyl ,, ...	100	+10·06	+11·28	+ 7·33	,,
Ethyl ,, ...	100	+23·11	+27·89	+33·62	,,
Methyl ,, ...	150	+11·4	+13·53	+11·53	,,
Ethyl ,, ...	150	+24·89	+30·62	+39·51	,,
Methyl acetyltartrate	90	+ 5·13	+ 4·71	− 1·34	,,
Ethyl ,, ...	90	+28·36	+35·13	+42·68	,,
Methyl diacetyltartrate ...	110	−13·27	−20·03	−46·76	,,
Ethyl ,, ...	110	+17·41	+20·33	+18·82	,,
Methyl ,, ...	150	− 5·82	− 9·91	−27·66	,,
Ethyl ,, ...	150	+23·29	+28·4	+33·56	,,
Methyl benzoyltartrate ...	30	+11·91	+11·43	− 2·06	,,
Ethyl ,, ...	30	+48·07	+59·17	+72·56	,,
Methyl ,, ...	150	+13·82	+15·32	+ 8·58	,,
Ethyl ,, ...	150	+40·46	+50·29	+65·43	,,
Methyl dibenzoyltartrate ...	150	−167·8	−236·1	−460·2	Compl
Ethyl ,, ...	150	−157·1	−221·5	−437·4	,,

1927, **60**, 2447), and it is noteworthy that the temperature–rotation curves are at maxima. On benzoylation a change of order occurs with displacement into the negative region (Freudenberg and Rhino, *Ber.*, 1924, **57**, 1547).

The *d*-malates afford an almost exact parallel, except that the benzoyl derivatives are in the positive region (Walden, *Z. physikal. Chem.*, 1895, **17**, 245; Frankland, J., 1899, **75**, 337).

The peculiar displacement of the methyl with respect to the ethyl ester was first noted by Frankland (*loc. cit.*; compare also the *o*-, *m*-, and *p*-toluoyl derivatives, in which this order persists).

The rule that a hydroxy-acid of "*d*" configuration shows a right displacement in passing from the methyl to the ethyl ester is broken by the benzoyl-lactates, the rotational values of which are far removed from the region of anomaly and in the negative region; it is also broken by the *d*-benzoylmalates and they are situated in the region of anomaly and exhibit positive rotation (Freudenberg and Noë, *Ber.*, 1925, **58**, 2404).

l-Glyceric acid ("*d*") obeys the rule for the esters of its acetyl derivative, but is exceptional with respect to those of its benzoyl derivative (Frankland and Price, J., 1897, **71**, 253). The di-*o*-, -*m*-, and -*p*-toluoyl derivatives are similar to the dibenzoyl esters in behaviour.

It is thus seen to be difficult to draw up a general rule connecting displacement and configuration for *iso*-esters, and esters of acetyl and benzoyl derivatives. A certain generality holds, however: when acetylation of the esters causes a displacement to the left, the order of the rotations is maintained in the benzoyl derivatives (*e.g.*, the mandelates and tartrates), and when it causes a displacement to the right, the order of the rotations is reversed in the benzoyl derivatives (*e.g.*, lactates and malates). In general, benzoylation of the esters causes a left displacement into the negative region, but the benzoylmalates are situated in the positive region, the methyl ester having suffered a right and the ethyl ester a left displacement.

In the case of the methyl and ethyl acetyltartrates, although the displacements are respectively left and right, yet a study of the dispersion and temperature–rotation diagrams shows that in both cases the rotational displacement has resulted in a more extended field of anomaly, the effect in both cases being similar. The corresponding benzoyl derivatives show rotationally right displacements (without change in order). The dispersion and temperature–rotation diagrams indicate that the methyl monobenzoyl ester has attained maxima for certain wave-lengths, whilst the ethyl ester has just passed maxima; here again the effects of benzoylation

are similar. Owing to the detailed data available with respect to these esters a deeper interpretation of rotational values has been possible, resulting in exact comparison in particular regions of anomaly.

Although similar displacements occur in certain derivatives of mandelic and tartaric acids, yet it should be noted that, in the former, increase of the acyl chain of both the methyl and ethyl esters produces displacements to the right (from the data given by Walden, *Z. physikal. Chem.*, 1895, **17**, 706), whereas in the latter, displacements to the left occur (from data given by Frankland and Wharton, J., 1899, **75**, 337), resulting in the methyl esters being carried progressively further into the negative region and the ethyl ester from the positive to the negative region. The mandelates are allied in this respect to the malates which are situated in the positive region, the molecular rotational displacements moving only slowly further into the positive region with increase of the acyl chain.

Comparative data for lactic acid are afforded by the *iso*butyl ester and its derivatives (Wassmer and Guye, *J. Chim. phys.*, 1903–4, **1**, 257), in which the molecular rotation passes through a maximum at the propionyl derivative:

$[M]_D$	+22·5	+91·2	+95·8	+82·7	
t	18°	20°	18·5°	19°	
	Ester.	Acetyl-	Propionyl-	Butyryl-	derivative.

The observations of Freudenberg and his collaborators with respect to certain derivatives of the amino-acids are of importance. The following data indicate a *right* rotational displacement on passage from the methyl to the ethyl ester, both compounds being of configuration denoted by "*l*":

Methyl acetyl-*l*-aspartate	$[M]_{5780}^{20°}$	−31°;	$[M]_{5780}^{100°}$	−25°
Ethyl ,, ,, ...	,,	−21°;	,,	−18° *
Methyl benzoyl-*l*-alanine	$[M]_{5780}^{19°}$	+13·7°		
Ethyl ,, ,, ...	$[M]_{5780}^{20°}$	+98·6° †		

* Freudenberg and Noë, *Ber.*, 1925, **58**, 2399.

† Freudenberg and Rhino, *Ber.*, 1924, **57**, 1547.

Thus this empirical method breaks down when applied to the naturally occurring amino-acids. Anomaly, however, is a true criterion for their configuration.

Rotatory Dispersion.

The dispersion ratios for the *n*-, *iso*-, and *tert*.-esters are sensibly constant as indicated in the table below.

Ester.	λ 6708.	λ 5893.	λ 5461.	λ 5086.	λ 4359.
		Dispersion ratios at 45°.			
n-Butyl	0·602	0·821	1	1·207	1·703
*iso*Butyl	0·598	0·820	1	1·203	1·715
tert.-Butyl	0·601	0·823	1	1·204	1·720
d-sec.-Butyl	0·588	0·823	1	1·210	1·843
		Dispersion ratios at 75°.			
n-Butyl	0·603	0·828	1	1·203	1·705
*iso*Butyl	0·602	0·821	1	1·195	1·708
tert.-Butyl	0·600	0·829	1	1·208	1·730
d-sec.-Butyl	0·590	0·820	1	1·210	1·868

The slight irregularity for the tertiary ester, particularly for 75° and λ 4359, was confirmed on a new preparation of the ester. The dispersion curves tend to diverge from the corresponding curves of the *n*- and *iso*-esters and to become steeper on proceeding into the violet end of the spectrum. Thus the substitution of branched chains for the normal chain has apparently little effect on the value of the dispersion ratios, as in the results obtained for the corresponding esters of lactic acid. The magnitudes of the ratios vary considerably on proceeding from the lactates to the mandelates.

The ratios for *d-sec.*-butyl *l*-mandelate show greatest divergence from an average value for light of short wave-length.

It is to be noted that the ratio $[\alpha]^{t}_{4359}/[\alpha]^{t}_{5461}$ lies above the minimum value 1·57 for cases of simple rotatory dispersion. All the esters exhibit normal and complex rotatory dispersion. The chief points of interest with regard to the dispersion diagrams are: (1) The curves obtained by plotting $1/\alpha$ against λ^2 show curvature; (2) increase of temperature decreases the rotation; (3) the dispersion curves are very nearly parallel, only slight convergency and divergency occurring at the red and blue ends of the spectrum, respectively; (4) no intersections take place in either the α–λ or [α]–λ curves; (5) the dispersion is allied to that of the lower normal esters of *l*-hexahydromandelic acid (Wood and Comley, *J.*, 1924, **125**, 2630), *i.e.*, it is similar in general character to that exhibited by certain of the *n*-alkyl *l*-lactates in the positive region. From a consideration of (3), (4), and (5), it is inferred that the esters are not in proximity to the region of anomaly.

The rotatory dispersion exhibited by *d-sec.*-butyl *l*-mandelate is a simple example of the superposition of the partial rotations of two asymmetric centres in a single molecule (the centres possessing rotations of opposite sign and different dispersion ratios). The esterification of mandelic acid, which has a high negative rotation ($[\alpha]^{20^\circ}_{D}$, in water, 156·8°), with *sec.*-butyl alcohol, which has a low positive rotation ($[\alpha]^{20^\circ}_{D}$ 13·56°), results in the formation of an ester showing a decrease of rotation compared with the other isomeric esters investigated, the effect not being marked enough to cause the

appearance of visual anomaly, and the dispersion data indicate the dominant centre to be the asymmetric mandelyl group. It follows, therefore, that the partial rotations of the two asymmetric centres should be of comparable magnitude for visual anomaly. This case is different from that of *d-sec.*-butyl *d*-lactate, in which the rotatory powers of the two centres are comparable and favourable for anomaly in the visible region.

Effect of Change of Temperature.

The esters are sensitive to temperature change, the change in rotatory power being more pronounced in the blue region of the spectrum; an increase in temperature causes a decrease in rotation. The temperature–rotation curves for the longer wave-lengths are nearly linear, but as the wave-length decreases the curvature increases uniformly. They form a series of curves converging to a small extent in the direction of increase of temperature; they are slightly convex and inclined to the axis of zero rotation. Curvature is most apparent in the *d-sec.*-butyl ester. Unsuccessful attempts were made with certain of these esters to see whether at higher temperatures a more definite change in curvature could be realised.

The temperature range over which the esters were investigated was comparatively small owing to the low decomposition and racemisation temperature, which occurred at 105—110°, for the *n*-, *iso*-, and *d-sec.*-esters, and at 95—100° for the tertiary ester.

EXPERIMENTAL.

Resolution of Mandelic Acid.—Mandelic acid was resolved by the precipitation and fractional crystallisation of its morphine salt (McKenzie, J., 1899, 75, 966) with the following modification. 50 G. of mandelic acid (1 mol.) were neutralised with 95 g. of morphine (1 mol.) in 400 c.c. of water and evaporated on a water-bath to a gum; while this was still warm, 400 c.c. of alcohol were added and the mixture was allowed to cool; addition of a nucleus of the pure active salt and vigorous stirring and scratching then precipitated the impure morphine *l*-mandelate, m. p. 185°, rising to 223—224° after two recrystallisations from absolute alcohol; $[\alpha]_D^{18°}$ — 110·5° in water ($c = 0·9499$; $l = 2$). Yield, 47 g. The alkaloid was precipitated from an aqueous solution of the salt with ammonia and filtered off, the acidified solution extracted with ether, the extract dried, the solvent distilled, and the acid recrystallised from benzene; m. p. 133·5°; $[\alpha]_D^{20°}$, in water, —157·2° ($c = 2·01$; $l = 2$). This was the highest rotation observed in a large number of resolutions.

Resolution by means of quinine was best effected from dilute

alcohol. Mandelic acid (7·6 g.; 1 mol.) and quinine (8·1 g.; ½ mol.) dissolved in 200 c.c. of 40% alcohol were gradually cooled to 0°. Crystallisation proceeded slowly, and the salt recrystallised from absolute alcohol had m. p. 180—181° (decomp.) and $[\alpha]_D^{20°}$, in alcohol, $-143·3°$ ($c = 0·579$; α $-1·66°$; $l = 2$). McKenzie (*loc. cit.*) gives 202° for the *l*-salt and 180° for the *d*-salt. The *l*-mandelic acid obtained after decomposition of the salt and recrystallisation from water had $[\alpha]_D^{20°}$ $-156·6°$ (c = approx. 2% in water); yield, 55%.

n-Butyl l-*Mandelate*.—Concentrated sulphuric acid (2·6 g.) was added carefully to a mixture of 8·7 g. of *l*-mandelic acid and 13 g. of *n*-butyl alcohol (b. p. 117°); the mixture was refluxed for 8 hours on a water-bath, diluted with dry ether, neutralised with potassium carbonate, filtered, dried over anhydrous sodium sulphate, and the ether evaporated. Excess of alcohol was removed at a low temperature in a vacuum. The *ester* was dissolved in light petroleum (b. p. 40—60°) and cooled in a freezing mixture; the resulting crystals were recrystallised eight times and obtained in long, colourless needles, m. p. 38·5° (corr.). Yield, 7·8 g. (62%) (Found: C, 69·05; H, 7·7; equiv. by saponification, 207·8. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%; equiv., 208·2).

Comparative data available for this ester are as follows:

	Smiles and Walker (*J. Physical Chem.*, 1909, 13, 580).	Present authors.
M. p.	31°	38·5°
$d_{4°}^{50°}$	1·0460	1·0443
$d_{4°}^{60°}$	1·0370	1·0355
$[M]_D^{50°}$	$-192·2°$	$-186·99°$
$[M]_D^{60°}$	$-187·4°$	$-181·79°$

Rotations were taken with a 1 dcm. tube. The rotatory dispersion is complex.

The ester decomposed at about 110°. Densities determined:

Temp.	39·1°	61·1°	80·0°	102·7°
$d_{4°}^{t°}$	1·0536	1·0346	1·0182	0·9983

$d_{4°}^{43·2°} = 1·0504$. $d_{4°}^{61·5°} = 1·0345$. $d_{4°}^{81°} = 1·0174$. $d_{4°}^{102·1°} = 0·9988$.

λ.	$[\alpha]_\lambda^{43·2°}$.	$[\alpha]_\lambda^{61·5°}$.	$[\alpha]_\lambda^{81°}$.	$[\alpha]_\lambda^{102·1°}$.
6708	$-67·02°$	$-63·61°$	$-60·00°$	$-56·67°$
6563	70·62	67·07	63·26	59·61
6438	73·88	70·20	66·49	62·40
6152	82·35	78·55	74·35	70·09
5893	91·77	87·37	82·90	78·92
5589	105·80	100·05	95·00	90·03
5461	111·71	105·79	100·10	95·31
5324	119·19	113·27	107·05	102·29
5086	134·32	127·38	120·50	115·04
4861	149·94	142·02	135·15	128·56
4678	164·03	155·73	148·22	141·25
4456	181·83	172·32	164·15	157·29
4359	190·21	180·03	171·62	164·90

iso*Butyl* l-*Mandelate*.—The preparation was similar to that of the normal ester [10 g. of *l*-acid, 15 g. of *iso*butyl alcohol (b. p. 106·5°), and 3 g. of sulphuric acid], and the crude ester purified as follows. A regulated current of dry air was drawn through a dilute solution of the ester in light petroleum (b. p. 40—60°), which was cooled in a freezing mixture. The gradual removal of the solvent caused crystallisation of the ester; eight to ten recrystallisations were necessary to give material of constant rotation and of m. p. 35·5° (corr.). Yield, 8·5 g. (60%) (Found: C, 69·1; H, 7·65; equiv., 208·4. Calc. for $C_{12}H_{16}O_3$: C, 69·2; H, 7·7%; equiv., 208·2). Walden (*Z. physikal. Chem.*, 1895, **17**, 706) gives $[M]_D^{20°}$ − 209°; $[\alpha]_D^{20°}$ −100·73°.

A 1 dcm. tube was employed for the measurements. The ester exhibits complex rotatory dispersion.

Above 105° decomposition of the ester was noted. Densities determined:

Temp.	38·5°	61·2°	80·1°	102·3°
$d_4^{t°}$	1·0536	1·0337	1·0173	0·9977

	$d_{4°}^{42°}$ = 1·0506.	$d_4^{59°}$ = 1·0357.	$d_4^{81°}$ = 1·0165.	$d_{4°}^{99°}$ = 1·0007.
λ.	$[\alpha]_\lambda^{42°}$.	$[\alpha]_\lambda^{59°}$.	$[\alpha]_\lambda^{81°}$.	$[\alpha]_\lambda^{99°}$.
6708	−74·30°	−70·90°	−66·94°	−63·56°
6563	78·20	74·92	70·18	66·67
6438	81·97	78·53	73·58	69·82
6152	91·90	87·75	82·01	77·31
5893	102·65	97·68	91·34	86·01
5589	117·76	111·87	104·40	98·57
5461	124·58	118·32	110·78	104·23
5324	134·02	126·77	118·32	111·54
5086	150·35	142·03	132·54	125·65
4861	167·72	157·86	147·66	140·90
4678	184·27	172·98	161·45	153·99
4455	206·52	193·31	180·03	170·95
4359	217·01	202·97	188·65	179·03

tert.-*Butyl* l-*Mandelate*.—To a mixture of *tert.*-butyl alcohol (10 g.; b. p. 83°/760 mm.), *l*-mandelic acid (10 g.), and 10 c.c. of light petroleum (b. p. 75—80°), sulphuric acid (3 g.) was added in the cold and the mixture refluxed on a water-bath for 4 hours; 4—5 volumes of dry, light petroleum (b. p. 40—60°) were then shaken with the reaction mixture, and the upper layer was neutralised with potassium carbonate, filtered, dried over anhydrous sodium sulphate, and the ether evaporated. The excess of alcohol was removed in a vacuum, and the *ester* recrystallised 8 times, as for the preceding ester, to a constant rotation and m. p. 65°. Yield 6·8 g. (45%) (Found: C, 69·4; H, 7·8%; equiv., 208·6). A peculiarity was noted in the behaviour of samples of the esters when

kept in a vacuum desiccator: the rotation increased and a compound of low m. p. was formed which rendered crystallisation of the ester difficult; this was most pronounced in the tertiary ester and may be due to the formation of a lactide or ether.

Rotations were taken in a 1 dcm. tube. The ester exhibits complex rotatory dispersion.

Decomposition was noted above 95°. Densities determined:

Temp.	19·0°	37·5°	59·6°	79·6°
$d_{4^\circ}^{t^\circ}$	1·0682	1·0520	1·0325	1·0146

	$d_{4^\circ}^{21^\circ}$ = 1·0665.	$d_{4^\circ}^{38·7^\circ}$ = 1·0507.	$d_{4}^{58·3^\circ}$ = 1·0335.	$d_{4}^{78·5}$ = 1·0157.
λ.	$[\alpha]_\lambda^{21^\circ}$.	$[\alpha]_\lambda^{38·7^\circ}$.	$[\alpha]_\lambda^{58·3^\circ}$.	$[\alpha]_\lambda^{78·5^\circ}$.
6708	−59·73°	−57·64°	−54·80°	−52·54°
6563	62·82	60·66	57·63	55·21
6438	65·86	63·63	60·47	58·08
6152	74·06	71·44	67·83	65·01
5893	82·70	79·53	75·55	72·32
5589	94·54	90·66	86·16	82·52
5461	100·20	96·03	91·48	87·46
5324	107·04	102·52	97·72	93·60
5086	121·11	116·02	110·20	105·63
4861	134·03	129·04	123·12	118·05
4678	146·65	141·20	135·02	129·98
4455	164·83	158·30	151·33	145·30
4359	172·40	165·75	157·85	151·64

d-sec.-*Butyl* l-*Mandelate*.—To a mixture of 8 g. of *d-sec.*-butyl alcohol (b. p. 99°/757 mm.; $[\alpha]_D^{20^\circ}$ + 13·56°) and 10 c.c. of light petroleum (b. p. 75—80°), cooled in ice and salt, sulphuric acid (2·6 g.) was added, followed by 8 g. of *l*-mandelic acid. The mixture was refluxed on a water-bath for 6 hours and the *ester* isolated in a similar way to the tertiary ester; after 2 fractionations it had b. p. 88°/0·05 mm. and $\alpha_D^{20^\circ}$ 77·50°. A further preparation gave the same result, and a third fractionation was unnecessary. Yield, approx. 6 g. (50%) (Found: C, 69·2; H, 7·6%; equiv., 208·4).

Hydrolysis of the ester. 4 G. of the ester were treated with caustic potash and steam-distilled; the recovered alcohol was converted into the hydrogen phthalate of m. p. 46—47°, $[\alpha]_D^{20^\circ}$ + 38·9° (m. p. of original hydrogen phthalate 48°, and $[\alpha]_D^{20^\circ}$ + 39·5° in alcohol). Acid hydrolysis and extraction with ether gave a specimen of acid which on recrystallisation once from benzene had m. p. 133°, $[\alpha]_D^{20^\circ}$ −156·3° (m. p. of original acid 133·5°, and $[\alpha]_D^{20^\circ}$ −156·8°).

A 0·5-dcm. polarimeter tube was employed, and the ester was found to exhibit complex rotatory dispersion. Decomposition was noted at 105—110°. Densities determined:

Temp.	3·0°	18·0°	43·5°	68·5°	93·0°
$d_{4°}^{t°}$	1·0746	1·0623	1·0410	1·0209	0·9992
	$d_{4°}^{4°}$ = 1·0742.	$d_{4°}^{19·8°}$ = 1·0607.	$d_{4°}^{49·8°}$ = 1·0360.	$d_{4°}^{68·2°}$ = 1·0207.	$d_{4°}^{91·4°}$ = 1·0014.
λ.	$[\alpha]_{\lambda}^{4°}$.	$[\alpha]_{\lambda}^{19·8°}$.	$[\alpha]_{\lambda}^{49·8°}$.	$[\alpha]_{\lambda}^{68·2°}$.	$[\alpha]_{\lambda}^{91·4°}$.
6708	−56·34°	−52·89°	−47·90°	−45·63°	−42·86°
6563	59·43	55·76	50·04	47·73	44·99
6438	62·30	58·49	52·94	50·29	47·35
6152	69·88	65·63	59·50	56·32	53·04
5893	77·85	73·12	66·51	62·96	59·11
5589	89·51	84·07	76·14	72·18	67·84
5461	94·75	89·06	80·93	76·55	71·98
5324	101·32	95·18	86·58	82·14	76·95
5086	114·58	107·74	97·88	92·62	87·03
4861	128·99	121·71	110·56	105·09	98·66
4678	143·79	135·92	123·51	117·15	110·20
4455	163·30	154·25	140·33	133·57	126·48
4359	173·02	163·21	149·03	141·78	135·06

Summary.

1. In the isomeric butyl mandelates, the *iso*butyl ester shows an ncrease and the *tert.*-ester a decrease of negative rotation when ompared with the *n*-ester. Pronounced decrease in rotation takes lace when there are two asymmetric centres of opposite sign in he molecule, but without visual anomaly. For visual anomaly he partial rotations of the two asymmetric centres should be of omparable magnitude.

2. All the esters exhibit normal and complex rotatory dispersion.

3. Increase of temperature causes a decrease in rotation of the sters. No maxima or minima occur in the temperature–rotation iagrams.

4. Comparison of the rotation data of the *n*-, *iso*-, and *tert.*-esters ffords no generalisation for relative configuration purposes.

5. Rotational displacements in related series are discussed as a uide to configuration.

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CLXXXVI.—*The Catalytic Hydrogenation of Different Types of Unsaturated Compounds. Part III. The Hydrogenation of Conjugated Systems.*

By SERGUEY V. LEBEDEV and ANASTASIA O. YAKUBCHIK.

Part II (this vol., p. 823) we classified conjugated systems accord- to their method of catalytic hydrogenation, and made a study of hydrogenation of isoprene as being representative of Type II— most complicated of the four types. It was also shown that a

diagram of the whole process could be constructed from a few suitably chosen experimental data. We have now studied three other compounds of the same type, *viz.*, di*iso*propenyl, divinyl, and piperylene and our former conclusions are confirmed and extended.

EXPERIMENTAL.

(A) Di*iso*propenyl.

A solution of pinacol (1 mol.) in acetic anhydride (4 mols.) was introduced drop by drop into warm acetic anhydride in which a small quantity of crystalline phosphoric acid was dissolved. Distillation gave a mixture of di*iso*propenyl and acetic acid, and redistillation over metallic sodium gave di*iso*propenyl, b. p. 69°, $d_{4°}^{20°}$ 0·7262, $d_{4°}^{0°}$ 0·7444 (yield, 85—90%).

The hydrogenation of di*iso*propenyl proceeds at a similar rate to that of isoprene, and the corresponding curve (Fig. 1; 1) is nearly the same, 68—70% of the hydrogen necessary for saturation being absorbed at a uniform velocity. The end of this stage is what we have called "the critical point of hydrogenation of the conjugated system" (*loc. cit.*), for it corresponds to the disappearance of this system. In the next stage the rate of absorption increases, and then falls abruptly to the third and last section. The proportions of hydrogen absorbed in the different sections * as calculated from Fig. 1 are:

Section	1	2	3
Hydrogen, %	69	22·5	8·5

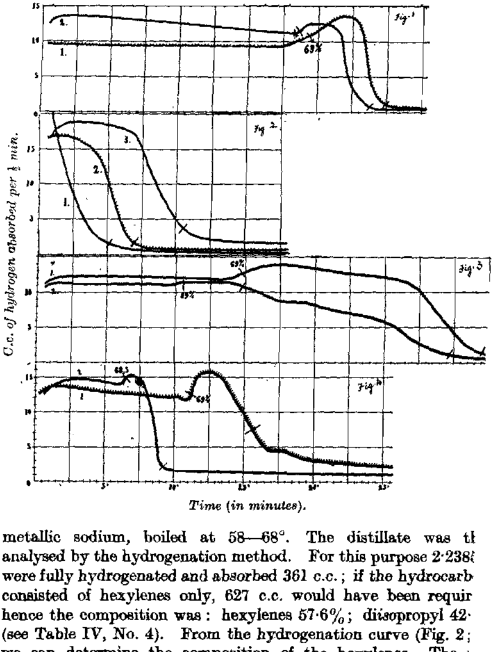
The formula of di*iso*propenyl, $CH_2{:}CMe{\cdot}CMe{:}CH_2$, indicates the following possibilities for the process of hydrogenation: (1) 1 : 2- or 3 : 4-Addition of 1 mol. to give *as.*-methyl*iso*propylethylene. (2) 1 : 4-Addition of 1 mol. to give tetramethylethylene. (3) Addition of 2 mols. of hydrogen, giving di*iso*propyl. It will be shown later that the second section of the curve corresponds to the hydrogenation of methyl*iso*propylethylene, and the third to that of tetramethylethylene. Before the critical point (68—70% of hydrogen absorbed) all three possible substances are formed simultaneously.

The Hydrogenation Process prior to the Critical Point.—In order to study the process of hydrogenation up to the critical point, we interrupted it after the addition of 25% and 50% of hydrogen, and investigated the products. Di*iso*propenyl was removed as a solid compound with sulphur dioxide as in the case of isoprene (*loc. cit.*),

* The sections of the curves are separated by dashes which are placed on the indefinite intermediate parts of the curve in such a position that these parts are divided in proportion to the velocities of hydrogenation on the horizontal portions concerned.

and the remaining products were estimated by our method of hydro-genation of mixtures.

25% *Hydrogenation.* To 17·4114 g. of di*iso*propenyl, 2527 c.c. o: hydrogen were added (see Table IV, No. 2), and the product wa: treated with sulphur dioxide at 0° and kept for 8 days. The liquic was distilled on a steam-bath into a vessel containing alkali at 0° and the hydrocarbon layer, when separated and distilled ove:



Time (in minutes).

metallic sodium, boiled at 58—68°. The distillate was tl analysed by the hydrogenation method. For this purpose 2·238(were fully hydrogenated and absorbed 361 c.c.; if the hydrocarb consisted of hexylenes only, 627 c.c. would have been requir hence the composition was: hexylenes 57·6%; di*iso*propyl 42· (see Table IV, No. 4). From the hydrogenation curve (Fig. 2; we can determine the composition of the hexylenes. The : section (up to the dash) pertains, as will be shown later, to met ... and the second to tetramethylethylene.

Table I are given the amounts of hydrogen absorbed in different sections of the curve and the calculated compositions of the reduction products; Table II shows the composition of the original product of hydrogenation.*

TABLE I.

	25% Hydrogenation.		50% Hydrogenation.	
	C.c. of H_2 absorbed.	Components, %.	C.c. of H_2 absorbed.	Components, %.
as.-Methyl*iso*propylethylene	98	15·5 } 57·5	173	38 } 61
Tetramethylethylene	263	42 }	105	23 }
Di*iso*propyl	0	42·5	0	39
Total	361	100	278·5	100

TABLE II.

Degree of hydrogenation.	25%.		50%.		69%.
	Exptl. data.	Data † from diagram.	Exptl. data.	Data † from diagram.	Exptl. data upon which diagram was based.
Di*iso*propenyl	64·9%	64%	28%	28%	0%
Di*iso*propyl	14·9	14	28	28	38
as.-Methyl*iso*propylethylene	5·4 } 20·2	16 } 22	27·4 } 44	32 } 44	45 } 62
Tetramethylethylene ...	14·8 }	6 }	16·6 }	12 }	17 }
Total	100	100	100	100	100

† See p. 2195.

50% *Hydrogenation.* To 14·228 g. of di*iso*propenyl, 4187 c.c. of hydrogen (1 mol.) were added. The hydrogenation product was freed from di*iso*propenyl as before, and kept saturated with sulphur dioxide for 10 days. When freed from the residue and distilled over metallic sodium, the hydrocarbons boiled at 57—68°. The composition of this mixture was investigated by the hydrogenation method: 1·5969 g. of substance absorbed 278·5 c.c. of hydrogen; if the hydrocarbons consisted of hexylenes only, 456·5 c.c. would have been required. The composition was therefore hexylenes 61%, di*iso*propyl 39% (see Table IV, No. 5).

The nature of hexylenes as determined by the examination of the two sections of the curve (Fig. 2; 2) leads to the results given in Table I, from which it is possible to deduce the composition of the product before its treatment with sulphur dioxide, having regard to the fact that at 50% hydrogenation the amount of di*iso*propyl

* The calculation is as follows: 100 Mols. of di*iso*propenyl require 50 mols. of hydrogen for 25% hydrogenation; if x mols. of hexylenes and y of di*iso*propyl have been formed, we have $x + 2y = 50$, and $x : y = 57·5 : 42·5$; hence $x = 20·2$; $y = 14·9$; and di*iso*propenyl (by diff.) $= 64·9$.

formed is equal to the quantity of di*iso*propenyl remaining in the mixture. The composition thus calculated is shown in Table II.

In order to decide which section of the curve relates to *as.*-methyl*iso*propylethylene, the product * of 50% hydrogenation (freed from di*iso*propenyl) was hydrogenated in admixture with a standard asymmetrically disubstituted ethylene, *viz.*, camphene; in Table III are shown (1) the amounts of hydrogen required in the various stages as calculated from the weight taken; (2) the amount of hydrogen actually absorbed by the hydrogenation (for numerical data, see Table IV, Expt. 6). Fig. 2, No. 3 is the corresponding curve. The table and the curve clearly show that camphene is hydrogenated in the first section of the curve; hence, according to the rule given in Part I (J., 1925, **127**, 417), *as.-methylisopropylethylene is also hydrogenated in this section and tetramethylethylene in the second.*

TABLE III.

C.c. of hydrogen absorbed in the sections of the hydrogenation curve for the mixture with camphene.

	Calc.	Found.
Section 1	108 + 201	312
Section 2	702	690
Total	810 + 201 = 1011	1002

69% *Hydrogenation (up to the critical point).* In Part II (*loc. cit.*) two methods of determining the critical point were described. (1) It corresponds to a break in the curve at the end of the first stage, such as is clearly seen at 69% hydrogenation in Figs. 1 and 4. (2) It can be deduced from the amount of di*iso*propenyl present at any moment of the process before the critical point, for the line representing this amount (see Fig. 5) cuts the axis of abscissæ at the percentage of hydrogenation corresponding to the critical point. In the product of 50% hydrogenation the amount of di*iso*propenyl was 28% (see Table II), and the continuation of the line through this point cuts the axis at 69·5%, in agreement with the value obtained by method (1).

As the conjugated system is no longer present beyond the critical point, the treatment of the product by sulphur dioxide becomes unnecessary, and the risk of isomerising the unsaturated substances (see Part II) is avoided. For the addition of the remaining 31% of hydrogen we have two well-defined sections of the curve: the first,

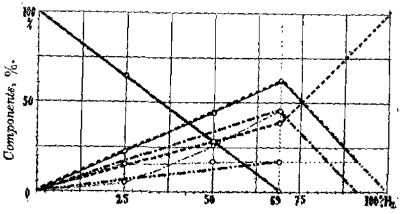
* The composition of the product used in this experiment differed from that mentioned in Table I. It was: saturated substance, 33; methyl*iso*propylethylene, 9; tetramethylethylene, 58%.

pertaining to methyl*iso*propylethylene, corresponds to 22·5% of hydrogen, and the second, relating to tetramethylethylene, to 8·5% (see p. 2191). The amounts of hexylenes corresponding to different sections are obtained by doubling the percentage of hydrogen absorbed over these sections. The composition calculated in this way is given in the third part of Table II.

General Survey of the Hydrogenation of Diisopropenyl.

The diagram representing the hydrogenation of di*iso*propenyl (Fig. 5) is based on the data given in Table II. It is similar to that of isoprene, as might be anticipated from the similarity of the two critical points, *viz.*, 68—70% for di*iso*propenyl and 69—71% for

FIG. 5.



——— *Diisopropenyl.* —·—·— as.-*Methylisopropylethylene.*
— — — *Diisopropyl.* —··—·· *Tetramethylethylene.*
===== *Total hexylenes.* O O *Quantities found experimentally.*

isoprene. A further resemblance is to be found in the fact that the experimentally determined quantities of di*iso*propenyl, di*iso*propyl, and *total* hexylenes lie on practically straight lines.

The lines for individual hexylenes, however, show breaks, doubtless owing to the circumstance that the relative quantities at 25% and 50% hydrogenation are altered by isomerisation during the treatment with sulphur dioxide, which, as shown later, rapidly converts *as.*-methyl*iso*propylethylene into tetramethylethylene. It is therefore improbable that the deviations are real; on the contrary, there is reason to believe that the curves should be straight lines, as shown by the thicker lines in the diagram. In Table II there are two sets of figures each for 25% and 50% hydrogenation; the experimental values are affected by the isomerisation, whereas the others were obtained from the diagram and are more likely to be correct.

Hydrogenation of Diïsopropenyl mixed with Standard Ethylenic Derivatives of Different Degrees of Substitution.

We undertook the hydrogenation of mixtures of di*iso*propenyl with ethylenic derivatives in order (1) to obtain sufficient hydrogenation curves to determine the position of the critical point, and (2) to determine the course of formation of the saturated molecules in the hydrogenation of a conjugated system. The numerical data and the results obtained are summarised in Tables IV, V, and VI. In Tables V and VI are shown (1) the amounts of hydrogen calculated for the three sections of the curve of di*iso*propenyl according to the scheme on p. 2191, and (2) the amounts of hydrogen which are actually absorbed in the sections of the curve in the hydrogenation of di*iso*propenyl in admixture with the standard ethylenic derivatives.

From Tables IV, V, and VI and the corresponding curves we note the following circumstances. The added standard ethylenic derivatives are generally hydrogenated after the critical point in the places determined by their degree of substitution. Thus, camphene is hydrogenated in the second section of the curve (Fig. 3; 1), together with methyl*iso*propylethylene, and tetramethylethylene in the third section (Fig. 4; 2). Crotonic acid (Fig. 3; 2) and trimethylethylene * (Fig. 4; 1), having no other substance of the same degree of substitution among the hydrogenation products, form a new section inserted between sections 2 and 3. Yet the *iso*propylethylene, added as a standard monosubstituted ethylene, is hydrogenated in the first section together with the conjugated system (Fig. 1; 2). The critical point retains its position and is clearly defined in every case.

The Formation of Fully Saturated Molecules prior to the Critical Point.—The hydrogenation in admixture with camphene requires a special study. Here two facts are of importance: (1) The beginning of the hydrogenation of an *as.*-disubstituted ethylene either formed in the actual process (methyl*iso*propylethylene) or added initially (camphene; methyl-*tert.*-butylethylene †), is distinctly separated from the end of the first section. (2) The whole of the *as.*-disubstituted standard added is hydrogenated after the

* In the case of this compound, the volume of hydrogen in the second section is increased at the expense of the third section (compare Table IV, No. 10 and Table VI). This occurred because the trimethylethylene used contained some *as.*-methylethylethylene which, being an *as.*-disubstituted ethylene, is naturally hydrogenated together with the similarly substituted methyl*iso*propylethylene. The curve is very long and only a part of the third section is included.

† The hydrogenation of di*iso*propenyl in admixture with *as.*-methyl-*tert.*-butylethylene has given the same results as with camphene.

TABLE IV.

Numerical data for diïsopropenyl hydrogenated totally, partially, and in admixture with monosubstituted derivatives.

[0·2 g. of Pt was used throughout except in Expts. No. 1 (0·3 g.) and No. 7 (0·25 g.).]

Expt. No.	Material.	Weight (g.).	C.c. of H_2 calc.	C.c. of H_2 obs.	Temp.	Press. (mm.).	Alcohol (c.c.).	Bath temp.	Curve No.
1	$C_6H_{10} + 2H_2$	0·8884	507	507	13°	758	35	0°	Fig. 1 (1)
2	$C_6H_{10} + \frac{1}{2}H_2$	17·4114	2527	2527	20	760	70	16·5	
3	$C_6H_{10} + H_2$	14·228	4187	4187	19	755	30	10	
4	$C_6H_{10} + \frac{1}{2}H_2$ freed from C_6H_{10}	2·2385	627	361	18	770	35	14·25	,, 2 (1)
5	$C_6H_{10} + H_2$ freed from C_6H_{10}	1·5969	456·5	278·5	16	750	35	14	,, 2 (2)
6	$C_6H_{10} + H_2$, freed from C_6H_{10}, + camphene	4·194 1·1574	810 201	1002	12	750	15	14	,, 2 (3)
7	Diïsopropenyl + *iso*propylethylene	0·0007 0·7498	332 252	580·5	19	765	30	17	,, 1 (2)
8	Diïsopropenyl + camphene	0·8840 1·5288	505 264	760	14	760	15	14	,, 3 (1)
9	Diïsopropenyl + crotonic acid	0·6100 0·8000	350 218·5	559	20	775	40	16	,, 3 (2)
10	Diïsopropenyl + trimethylethylene	0·6930 0·4910	403 165·5	555	21	770	30	17·5	,, 4 (1)
11	Diïsopropenyl + tetramethyl-ethylene	0·4041 0·3597	263 100	357	17	770	15	14	,, 4 (2)

TABLE V.

C.c. of hydrogen absorbed in the sections of the diïsopropenyl curve when hydrogenated in admixture with :

Section.	*iso*Propyl-ethylene. Calc.	*iso*Propyl-ethylene. Found.	Camphene. Calc.	Camphene. Found.	Tetramethyl-ethylene. Calc.	Tetramethyl-ethylene. Found.
1. Conjugated system	229 + 252	475	350	360	180	178
2. Methyl*iso*propyl-ethylene	75	80	110 + 264	358	58	59
3. Tetramethyl-ethylene	28	25	45	42	25 + 100	120
Total	332 + 252	580	505 + 264	760	263 + 100	357
	584		769		363	

TABLE VI.

C.c. of hydrogen absorbed in the sections of the diïsopropenyl curve when hydrogenated in admixture with :

	Crotonic acid. Calc.	Crotonic acid. Found.	Trimethyl-ethylene. Calc.	Trimethyl-ethylene. Found.
Section 1. Conjugated system	242	230	278	277
,, 2. Methyl*iso*propylethylene	77	85	91	105·5
Section of the components added	—	213	—	135·5
,, 3. Tetramethylethylene	31	31	34	37
Total	350	559	403	555

critical point, and therefore does not alter the amount of fully saturated molecules formed before this point. This suggests that the fully saturated molecules formed before the critical point are not formed directly from the component to which the section relates, but from the conjugated system by addition of 2 mols. of hydrogen, either simultaneously or in such a rapid succession as to appear to be so.

Hence, of the two assumptions made in Part II (this vol., p. 834), the second is obviously correct.

Isomerisation of as.-*Methyl*iso*propylethylene by the Action of Sulphur Dioxide.*

We stated above (p. 2194) that the use of sulphur dioxide caused an isomerisation which affected the apparent composition of the hydrogenation products of di*iso*propenyl. In order to demonstrate this, the 50%-hydrogenation product, freed from di*iso*propenyl, was saturated with sulphur dioxide at 0°, and kept in a sealed tube at 100° for 3 days. The resulting hydrocarbons were freed from sulphur dioxide and analysed by the hydrogenation method: 2·049 g. absorbed 352 c.c., whereas 577 c.c. of hydrogen would have been required if the hydrocarbons contained hexylenes only; hence the composition was: hexylenes 61%, di*iso*propyl 39%. The hydrogenation curve has two sections: in that corresponding to methyl*iso*propylethylene 44 c.c. were absorbed, equivalent to 7·5% of this hydrocarbon, and the absorption of 308 c.c. in the other section indicated 53·5% of tetramethylethylene.

Comparison of these proportions with those for the original material (Table 1) shows a large decrease (38 to 7·5%) for methyl*iso*propylethylene and a corresponding increase (23 to 53·5%) in tetramethylethylene. Moreover, these changes are much more extensive than those involving the amylenes derived from isoprene (see Part II, p. 835).

(B) *Divinyl.*

Divinyl, prepared by pyrogenetic decomposition of naphtha, was converted to the tetrabromide (m. p. after recrystallisation 113—115°), regenerated by zinc in alcoholic solution, and collected over saturated brine. A measured volume (usually 200—300 c.c.) was dissolved in alcohol containing platinum-black and hydrogenated at 0°, the amount of divinyl taken being calculated from the volume of hydrogen absorbed. The hydrogenation curve is given in Fig. 7.

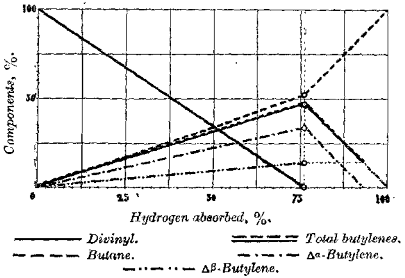
In the hydrogenation of divinyl, $CH_2{:}CH{\cdot}CH{:}CH_2$, three products can be formed, *viz.*, *n*-Δ^{α}- and Δ^{β}-butylene and butane. The rules given in Part I (*loc. cit.*) postulate three sections on the curve, and these can, in fact, be observed. The first, relating to the conjugated

system, ends at the critical point; the second pertains to Δ^{α}-, and the third to Δ^{β}-butylene. The presence of the 1 : 4 hydrogenation product proves that divinyl belongs to our Type II of conjugated systems. The critical point on the curve is at 76% of hydrogenation. The amounts of hydrogen absorbed in the different sections as calculated from Fig. 7 are:

Section	1	2	3
Hydrogen, %	76	17	7

Calculation from the hydrogen absorbed in the sections of the curves for divinyl in admixture with trimethylethylene (Fig. 8; 3) and with tetramethylethylene (Fig. 9; 2) gives similar figures. These two offer a good example for such a calculation, for on both curves all

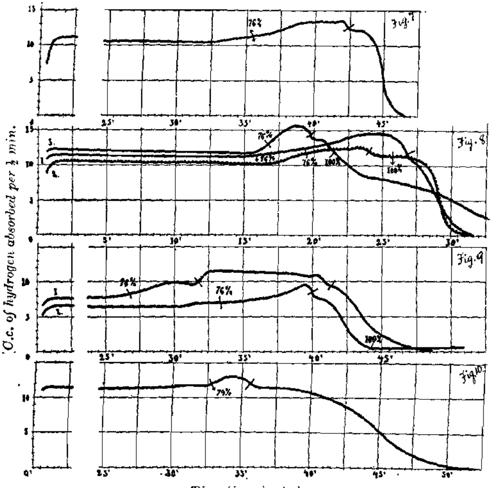
FIG. 6.



the divinyl is hydrogenated before the admixed substances. The figure 100% on these curves shows the point where the hydrogenation of divinyl is completed. The first of these curves shows clearly all the three sections; on the second the limits of the third section are very clearly marked. The composition of the hydrogenation product at the critical point, as calculated from the amounts of hydrogen absorbed, is: Divinyl, 0; butane, 52; Δ^{α}-butylene, 34; Δ^{β}-butylene, 14%; and Fig. 6 is constructed from these values.

Hydrogenation of Divinyl in Admixture with Monoethylenic Derivatives of Different Degrees of Substitution.—The curves in Figs. 7, 8, and 9 represent the hydrogenation of divinyl in admixture with ethylenic derivatives, and, in conjunction with the data of Tables VII and VIII, they provide the material necessary for following the course of the process. Both for divinyl alone and for its mixtures

the critical point is at 76% of hydrogenation. As in the case of other conjugated systems of Type II, the position of the critical point is not always clearly marked. The curve for the mixture with Δ^{β}-butylene (Fig. 8; 2) is very similar to that of pure divinyl (Fig. 7), but is more prolonged in the last section. The dash marked 100% on the curves indicates the point where, by calculation, divinyl is consumed and hydrogenation of the admixed component begins.



Time (in minutes).

(C) *Piperylene.*

Piperylene, $CH_2:CH\cdot CH:CH\cdot CH_3$, was obtained from piperidi by Hofmann's method (*Ber.*, 1881, **14**, 664); it had b. p. 41·5 [illegible] 0·6852. In spite of its unsymmetrical nature, piperylene c yield only two pentenes on hydrogenation, for the 1 : 2 a : 4 addition of 1 mol. of hydrogen both lead to the sa -methylethylethylene. It is therefore impossible to determ whether 1 : 4-addition actually occurs, but the properties piperylene (*e.g.*, its tendency to polymerise, and its energe

TABLE VII.

Numerical data for divinyl hydrogenated alone and in admixture with monoethylenic derivatives.

(Bath temperature, 0°; weight of Pt, 0·2 g.; vol. of alcohol, 50 c.c.)

Expt. No.	Material.	Vol. (c.c.).	Weight (g.).	C.c. of H_2 calc.	C.c. of H_2 obs.	Temp.	Press. (mm.).	Curve No.
1	Divinyl	490		980	980	17°	765	Fig. 7
2	Divinyl + *iso*propylethylene	223	0·7606	446 + 257	705	17	760	„ 8 (1)
3	Divinyl + Δ^{β}-butylene	266 80		532 + 80	600	18	760	„ 8 (2)
4	Divinyl + camphene	266	1·2098	532 + 211	734	19	765	„ 9 (1)
5	Divinyl + trimethylethylene	264	0·5138	528 + 173	697	18	765	„ 8 (3)
6	Divinyl + tetramethylethylene	287	0·210	574 + 59	623	18	760	„ 9 (2)

TABLE VIII.

C.c. of hydrogen absorbed in the sections of the curve when divinyl is hydrogenated in admixture with:

Section.	*iso*Propyl-ethylene. Calc.	Found.	Δ^{β}-Butylene. Calc.	Found.	Camphene. Calc.	Found.	Trimethyl-ethylene. Calc.	Found.	Tetramethyl-ethylene. Calc.	Found.
1	339	377	405·5	390	419	403	416·5	397	435·5	436
2	76 + 257	289	81	90·5	97	89	93·5	88	97·5	100
A *	—	—	—	—	211	216	—	—	—	—
3	31	39	37·5 + 80	120·5	39	54	38	42	40	40
B *	—	—	—	—	—	—	173	170	59	53
Total	446 + 257 = 703	705	524 + 80 = 604	601	763	762	721	697	632	629

* The sections thus denoted are due to substances which, in the absence of similarly substituted compounds among the products of hydrogenation, have formed their own sections.

reaction with sulphur dioxide) would suggest that some of the *s.*-methylethylethylene is formed in this way.

Piperylene evidently belongs to our Type II of conjugated systems. Its hydrogenation curve (Fig. 10) has three sections: that before the critical point (74% hydrogenation) is nearly horizontal; the second, due to propylethylene, corresponds to the more rapid absorption of 6·5% of hydrogen; and the third (19·5% of hydrogen) relates to *s.*-methylethylethylene (see Table X).

The amounts of hydrogen absorbed in the corresponding sections of the hydrogenation curves of piperylene in admixture with different derivatives of ethylene give nearly similar figures, the critical point usually corresponding to 72% hydrogenation (see Table IX).

The figures of the last column serve to calculate the composition of the hydrogenation product at the critical point. The amount of the particular pentene corresponding to each section is obtained by doubling the percentage of hydrogen absorbed over that section;

TABLE IX.

Percentages of hydrogen absorbed in the sections of the curves for piperylene.

No. of Fig. and curve	10.	12 (1).	12 (2).	12 (3).	13 (2).	Mean.
Section 1	74	73—75	72	72	72	73
„ 2	6·5	9—7	8	8	8	7·5
„ 3	19·5	18	20	20	20	19·5

the amount of pentane is obtained by difference. The composition thus calculated is: Piperylene, 0; propylethylene, 15; *s.*-methylethylethylene, 39; pentane, 46%. From these values in conjunction with Table IX, Fig. 11 is plotted by the method used in the case of di*iso*propenyl (Fig. 5).

FIG. 11.

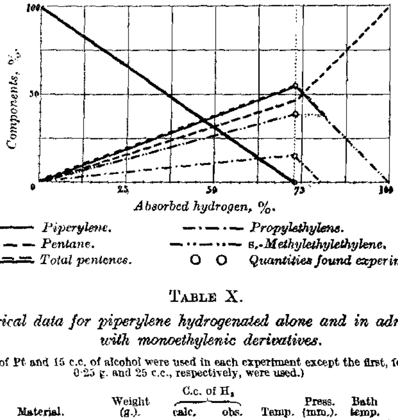


TABLE X.

Numerical data for piperylene hydrogenated alone and in admixture with monoethylenic derivatives.

(0·2 G. of Pt and 15 c.c. of alcohol were used in each experiment except the first, for which 0·25 g. and 25 c.c., respectively, were used.)

Expt. No.	Material.	Weight (g.).	C.c. of H_2 calc.	C.c. of H_2 obs.	Temp.	Press. (mm.).	Bath temp.	Curve No.
1	Piperylene	1·4539	1022	1015	14°	750	12·75°	Fig. 10
2	Piperylene Safrole	0·4515 1·3050	316 192	504	15	757	13·75	„ 12 (1)
3	Piperylene Camphene	0·4819 1·0038	331·5 172	491	15	767	14·25	„ 12 (2)
4	Piperylene Anethole	0·4287 2·9340	304 480	760	16	745	13·5	„ 12 (3)*
5	Piperylene Methylheptenone	0·4940 1·1224	344 210	542	13	755	10·5	„ 13 (1)*
6	Piperylene Tetramethylethylene	0·5881 0·2697	409 76	484·5	16	758	13·5	„ 13 (2)*

* A dash marked *100%* on these curves indicates the point where piperylene is consumed and the hydrogenation of the admixed substance begins.

Hydrogenation of Piperylene Mixed with Standard Ethylenic Derivatives of Different Degrees of Substitution.—We have examined a number of mixtures of piperylene with ethylenic derivatives of different degrees of substitution. The numerical data for these mixtures are in Tables X and XI. The construction of Table XI is similar to that of Table V.

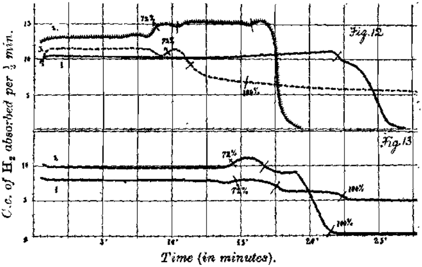


TABLE XI.

	Safrole.		Camphene.		Anethole.		Methyl-heptenone.		Tetramethyl-ethylene.	
Section	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.
1 } 2 }	255+192	454	242	235	222	213	251	240	290	292
			25	27	23	22	26	30	31	32
A	—	—	172	164	—	—	—	—	—	—
3	61	30	64	65	50+480	530	67	70	70	86
B	—	—	—	—	—	—	210	202	76	74
Total	316+192	504	332+172	491	304+480	765	344+210	542	409+76	484
	508		504		784		554		485	

From Tables X and XI the following facts emerge. (1) In the mixture of piperylene with safrole (a monosubstituted ethylene) the critical point is not clearly marked, for the safrole is partially hydrogenated in the first section (Fig. 12; 1). (2) The mixture with camphene gives a peculiar curve, for this *as.*-disubstituted ethylene has no pentene of the same degree of substitution among the products of hydrogenation; hence it forms an independent section (A) on the curve. (3) Anethole (Fig. 12; 3) and *s.*-methylethylethylene, being of the same degree of substitution, hydrogenate simultaneously. (4) Methylheptenone (Fig. 13; 1) and tetramethylethylene (Fig. 13; 2), like camphene, form independent sections (B). These derivatives of ethylene are to be found in the last sections of the curves in the places determined by their degree of substitution.

Summary.

(1) The study of the hydrogenation of di*iso*propenyl confirms and extends the general conclusions previously drawn from the study of isoprene.

(2) The amounts of all the components formed during the process of hydrogenation are shown in the hydrogenation diagram of Type II of conjugated systems as straight lines joining the zero point of the diagram with the corresponding points lying on the ordinate of the "critical point of hydrogenation."

(3) Saturated compounds are formed before the critical point is reached, because some molecules add two molecules of hydrogen simultaneously.

(4) The mono-ethylenic derivatives of different degrees of substitution, either formed in the process of hydrogenation or added initially, are hydrogenated after the critical point in places determined by their degrees of substitution. The mono-substituted ethylenes do not follow this rule, but hydrogenate partially or completely before the critical point.

(5) Piperylene and divinyl belong to Type II of conjugated systems. Diagrams are constructed showing the whole course of hydrogenation of these hydrocarbons.

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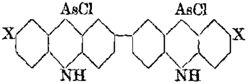
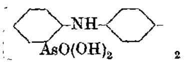
CCLXXXVII.—10-*Chloro-5 : 10-dihydrophenarsazine and its Derivatives. Part VI. Compounds containing Two Nitrogen and Two Arsenic Atoms in Six- and Five-ringed Systems.*

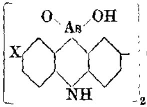
By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON

BY employing and extending the methods of preparation an synthesis described in previous papers (J., 1926, 450, 464, 2241; 192 247, 2499), compounds of the type I (X = H or Me) can be obtaine If, for example, benzidine (1 mol.) be condensed with *o*-brom phenylarsinic acid (2 mols.), 4 : 4-*bis*(*diphenylamine-2'-arsinic aci* (II) is obtained. This acid when reduced with sulphur dioxide i the presence of alcohol, hydrochloric acid, and a trace of iodine readily converted into 2 : 2'-*bis*(*10-chloro-5 : 10-dihydrophenarsazin* (I; X = H). The compound so obtained appears to be identic with that prepared by condensing *NN'*-diphenylbenzidine (1 mo with arsenious chloride (2 mols.). The only means of compari these two products is by microscopic examination, since they a

insoluble and their melting points cannot be determined in the ordinary way. By the methods already described, the chloro-

(I.) 

(II.) 

 (III.)

compound (I; X = H) has been oxidised to 2 : 2'-*bis*(*phenarsazinic acid*) (III; X = H), and from the latter the corresponding *bromo*-compound is readily obtained by the usual method of reduction.

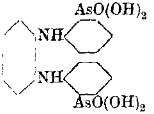
The condensation of *NN'*-di-*p*-tolylbenzidine with arsenious chloride gave 2 : 2'-*bis*(10-*chloro*-8-*methyl*-5 : 10-*dihydrophenarsazine*) (I; X = Me), from this 2 : 2'-*bis*(8-*methylphenarsazinic acid*) (III; X = Me) was obtained by oxidation, and the chloro-, *bromo*-, and *iodo*-compounds were prepared from the acid by reduction.

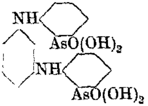
The above halogen compounds are intensely coloured, do not melt below 320°, and are practically insoluble in all the usual organic solvents. An acid of the type (II) can be recrystallised from dilute acetic acid, but acids of the type (III; X = H or Me) are insoluble in all solvents. They can, however, be purified conveniently through their crystalline disodium salts. This makes it possible to obtain the reduced halogen derivatives from them in a state of purity and, in the case of the chloro-compounds (I), these can be compared with the products of condensation of arsenious chloride and the di-secondary amines.

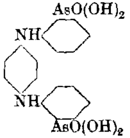
o-Bromophenylarsinic acid condensed with *o*-, *m*-, and *p*-phenylenediamines to give (IV) 1 : 2-, (V) 1 : 3-, and (VI) 1 : 4-*phenylenediaminodi*-o-*phenylarsinic acid*, respectively, but only the condensation with *m*-phenylenediamine was really satisfactory. The compound (IV) could not be purified and was reduced immediately in the presence of hydrochloric acid to 5 : 8-*dichloro*-13 : 14* : 5 : 8-*tetrahydro*iso*benzarsazinephenarsazine* (VII). This is the only possible constitution of a compound formed in this way. Owing to its sparing solubility, this compound could not be purified in the

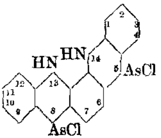
* For simplicity, it is preferred for these complex compounds to write the numbers of the hetero-atoms of lower atomic weight before those of the hetero-atoms of higher atomic weight in spite of the ordinary rule of order of numbering. This system is adhered to throughout this paper.

ordinary way, but by oxidising it to the diarsinic acid, freeing the latter from non-acidic impurities by solution in sodium hydroxide,

(IV.) 

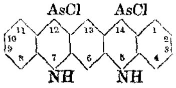
 (V.)

(VI.) 

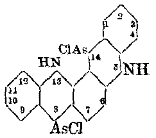
 (VII.)

and again reducing the precipitated acid, it was obtained in a reasonable state of purity. Contrary to expectation, this compound was not produced by condensing *NN'*-diphenyl-*o*-phenylenediamine (1 mol.) (Clemo, Perkin, and Robinson, J., 1924, **125**, 1780; Gibson and Johnson, this vol., p. 1988) with arsenious chloride (2 mols.), but the preliminary change in colour noticed might indicate the formation of an intermediate compound (compare Burton and Gibson, J., 1926, 454).

After purification by crystallisation from acetic acid, the diarsinic acid (V), when reduced in the presence of hydrochloric acid, yielded without difficulty a compound which can have either formula (VIII) or (IX). The product was highly crystalline and bright yellow. It

(VIII.) 

12 : 14-*Dichloro*-5 : 7 : 12 : 14-*tetra-hydrobenzarsazinephenarsazine.*

 (IX.)

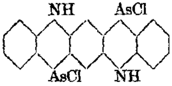
8 : 14-*Dichloro*-5 : 13 : 8 : 14-*tetra-hydrobenzarsazinephenarsazine.*

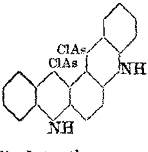
differed from the bright red compound, obtained by condensin pure *NN'*-diphenyl-*m*-phenylenediamine (1 mol.) with arseniou chloride (2 mols.) under the usual conditions, not only in colour bu also in crystalline form when viewed under the microscope. Th latter condensation product could also have a constitution represente by either (VIII) or (IX). When these two dichloro-compoun were separately oxidised to the diarsinic acids and these aci

separately reduced back to dichloro-compounds, products having the same colour (yellow) but different properties were obtained. The insolubility of the compounds and the absence of melting points, however, prevented absolute comparisons being made. In spite of the apparent differences between the two dichloro-compounds, specimens of the diarsinic acid [5 : 7 : 12 : 14(or 5 : 13 : 8 : 14)-*benzarsazinicphenarsazinic acid*] prepared from both, when purified through the highly crystalline *disodium salt*, appeared to be identical. From this acid, by reduction in the presence of hydrobromic acid and hydriodic acid respectively, the sparingly soluble, highly crystalline, and coloured *dibromo-* and *di-iodo*-compounds were easily obtained.

When the above diarsinic acid was treated with hypophosphorous acid, no reduction took place until iodine was added, and the substance then precipitated was not the cacodyl compound but the above di-iodo-compound. The necessity for the presence of iodine (or hydriodic acid) for reduction of quinquevalent arsenic in organic compounds by hypophosphorous acid to take place has been pointed out by previous workers.

NN'-Diphenyl-*p*-phenylenediamine (1 mol.) condenses readily with arsenious chloride (2 mols.) and the compound produced may be either 7 : 14-*dichloro*-5 : 12 : 7 : 14-*tetrahydrobenzarsazinephenarsazine* (X) or 13 : 14-*dichloro*-5 : 8 : 13 : 14-*tetrahydrobenzarsazinephenarsazine* (XI). The product appeared to be homogeneous,

(X.) 

 (XI.)

and being sparingly soluble, was oxidised to the corresponding 5 : 12 : 7 : 14(or 5 : 8 : 13 : 14)-*benzarsazinicphenarsazinic acid*, which again was purified through its *disodium* salt. The acid when reduced in the presence of hydrochloric acid gave the above-mentioned dichloro-compound, an orange-red, highly crystalline substance which, like the isomeric substances, does not melt below 320°. Similarly, the *dibromo*-compound with analogous properties was obtained by reducing the acid in the presence of hydrobromic acid, but the di-iodo-compound could not be obtained pure.

The work now described emphasises the highly crystalline nature and intense colour of the homologues of 10-chloro-5 : 10-dihydrophenarsazine and of the corresponding bromo- and iodo-compounds,

even when these derivatives possess a much more complicated structure which renders them insoluble and high-melting solids.

EXPERIMENTAL.

4 : 4-*Bis(diphenylamine-2′-arsinic acid)* (II).—A mixture of benzidine (3·45 g.; 1 mol.), o-bromophenylarsinic acid (11·3 g.; 2 mols.), anhydrous potassium carbonate (8·8 g.), amyl alcohol (40 c.c.), and a trace of copper powder was boiled under reflux for 5 hours; the product was steam-distilled to remove amyl alcohol and filtered while hot. On acidifying the filtrate with dilute hydrochloric acid, a discoloured acid was precipitated. This was obtained as a white powder, unmelted at 320°, by recrystallisation from dilute acetic acid (Found : As, 25·3. $C_{24}H_{22}O_6N_2As_2$ requires As, 25·7%).

2 : 2′-*Bis*(10-*chloro*-5 : 10-*dihydrophenarsazine*) (I; X = H).—(*a*) The preceding compound (crude, 1·2 g.), dissolved in a hot mixture of alcohol (25 c.c.) and hydrochloric acid (20 c.c.) to which a trace of iodine had been added, was reduced by passing sulphur dioxide for a few minutes. The precipitated *chloro-compound* was washed with alcohol and ether and dried at 120° (Found : Cl, 12·7 $C_{24}H_{16}N_2Cl_2As_2$ requires Cl, 12·8%).

(*b*) *NN′*-Diphenylbenzidine (m. p. 250°; from toluene) wa prepared from diphenylamine by the method described by Wielan and Wecker (*Ber.*, 1922, **55**, 1804) for the preparation of *NN′*-di *p*-tolylbenzidine; yield, 60%. The method described by Wielan and Müller (*Ber.*, 1913, **46**, 3296) gives a poor yield, as Marqueyr and Muraour (*Bull. Soc. chim.*, 1914, **15**, 186) have shown.

A mixture of *NN′*-diphenylbenzidine (23·1 g.; 1 mol.), arsenio chloride (27·8 g.; 2·2 mols.), and o-dichlorobenzene (100 c.c.) w boiled under reflux for 5 hours. (The mixture while still co developed a greenish-blue coloration: this has been frequent noticed in other condensations of this type and it may indicate t formation of a primary addition compound which is subsequent transformed into the ring condensation product; compare Burt and Gibson, J., 1926, 454.) Hydrogen chloride was freely evolv as soon as boiling commenced, and solid matter began to separa after about 30 minutes. The liquid was filtered while hot, t residue washed several times with hot o-dichlorobenzene to remo unchanged soluble materials, and the last trace of o-dichlorobenze removed from the product by heating at 160° for a short time. this condensation, it is important that carefully purified materi should be used; otherwise, highly coloured by-products are form and these render the purification of the main product matter of considerable difficulty. Yield, 58% (Found : As, 2 $C_{24}H_{16}N_2Cl_2As_2$ requires As, 27·1%).

2 : 2′-*Bis*(10-*chloro*-5 : 10-*dihydrophenarsazine*) formed by either of the above methods is a pale orange-yellow, microcrystalline powder, insoluble in all the usual organic solvents and such solvents as acetylene tetrachloride, *o*-dichlorobenzene, and nitrobenzene. It is slightly soluble in boiling naphthalene and crystallises from it in minute prisms on cooling. It remains unmelted at 325°.

(*c*) 2 : 2′-Bis(10-chloro-5 : 10-dihydrophenarsazine) was also prepared from 2 : 2′-bis(phenarsazinic acid) by a similar method to that used for the corresponding bromo-compound (see below).

2 : 2′-*Bis*(*phenarsazinic acid*) (III; X = H).—The use of chloramine-T (Burton and Gibson, J., 1924, **125**, 2275) for the oxidation of the preceding compound was impracticable because of the insolubility of the latter in acetone or water. 2 : 2′-Bis-(10-chloro-5 : 10-dihydrophenarsazine) (5 g.) was boiled with acetic acid (100 c.c.) in order to obtain the substance in a fine state of division. To the cooled suspension, hydrogen peroxide (20 vol.; 16 c.c.) was added and the mixture carefully heated to boiling. The colour of the chloro-compound changed to greyish-brown and in about 5 minutes oxidation was completed. (Because of their insolubility in acetic acid, oxidation of the chloro-compounds described in this communication does not proceed so readily and completely as in the case of the substances previously described; compare J., 1927, 2514.) Water (250 c.c.) was added to the cooled mixture and the solid matter was filtered off, well washed with water, and boiled with dilute aqueous sodium hydroxide. The solution obtained was filtered from non-acidic substances and treated with 20% aqueous sodium hydroxide until the hot, deep brown solution began to deposit the colourless crystalline *disodium* salt. This was filtered off when cold, well drained on the filter, dissolved in a small quantity of hot water, and reprecipitated as before with 20% sodium hydroxide solution. The disodium salt prepared in this way was obtained in short colourless needles, slightly soluble in cold water and more soluble in hot. For analysis, it was well washed with ice-cold water and dried at 160—165° (Found: Na, 7·6. $C_{24}H_{16}O_4N_2As_2Na_2$ requires Na, 7·8%). From a solution of the disodium salt in warm water, dilute hydrochloric acid precipitated 2 : 2′-*bis*(*phenarsazinic acid*) as a white and somewhat gelatinous precipitate (3·5 g.). It was washed with water and dried at 140—145° (Found: As, 27·3. $C_{24}H_{18}O_4N_2As_2$ requires As, 27·35%).

2 : 2′-Bis(phenarsazinic acid) is a white amorphous powder insoluble in the ordinary organic solvents and remains unmelted at 325°. As it was insoluble in a hot mixture of alcohol and hydrochloric acid, attempts to prepare a hydrochloride were unsuccessful. The potassium salt resembles the sodium salt; the magnesium,

calcium, and barium salts are white microcrystalline precipitates; the mercurous and mercuric salts are heavy white precipitates, the latter somewhat crystalline; the silver salt is a white curdy precipitate soluble in ammonia; and the cupric salt is a pale greenish-blue, curdy precipitate. The acid itself is soluble in ammonia, but, being such a weak acid, is precipitated on boiling, ammonia escaping. Attempts to reduce the acid in acetic acid suspension to a cacodyl compound by means of hypophosphorous acid were unsuccessful.

2 : 2′-*Bis*(10-*bromo*-5 : 10-*dihydrophenarsazine*) (formula as I) was prepared by reducing with sulphur dioxide a suspension of 2 : 2′-bis-(phenarsazinic acid) (1·8 g.) in a hot mixture of alcohol (20 c.c.) and hydrobromic acid (const. b. p.; 12 c.c.) to which a trace of iodine had been added, an orange-yellow colour being developed; the precipitate was washed with alcohol and dried at 140° (Found : Br, 24·7. $C_{24}H_{16}N_2Br_2As_2$ requires Br, 24·9%).

2 : 2′-*Bis*(10-*chloro*-8-*methyl*-5 : 10-*dihydrophenarsazine*) (I; X = Me) was prepared from arsenious chloride (10·5 g.), *NN*′-di-*p*-tolylbenzidine [prepared according to the method of Wieland and Wecker (*loc. cit.*) and obtained as colourless plates, m. p. 234°, much more soluble in toluene than *NN*′-diphenylbenzidine] (9·5 g.), and *o*-dichlorobenzene (38 c.c.) as described for 2 : 2′-bis(10-chloro-5 : 10-dihydrophenarsazine); yield, 64%. It was obtained in small orange-red crystals (Found : Cl, 12·4. $C_{26}H_{20}N_2Cl_2As_2$ requires Cl, 12·2%).

It was also prepared by reducing with sulphur dioxide a hot suspension of 2 : 2′-bis(8-methylphenarsazinic acid) (1·2 g.; see below) in alcohol (25 c.c.) and hydrochloric acid (20 c.c.) containing a trace of iodine. Owing to the insolubility of the acid and of the chloro-compound it was necessary to heat the mixture for 30 minutes on the water-bath and to shake it frequently in order to obtain complete reduction. The product was washed with alcohol-hydrochloric acid and with alcohol and dried at 140° (Found : Cl, 12·1. $C_{26}H_{20}N_2Cl_2As_2$ requires Cl, 12·2%).

2 : 2′-*Bis*(8-*methylphenarsazinic acid*) (III; X = Me) was prepared in 64% yield by oxidising the preceding compound (9·5 g.) in acetic acid (150 c.c.) suspension with hydrogen peroxide (20 vol.; 32 c.c.) as described for 2 : 2′-bis(phenarsazinic acid). It was purified through its *disodium* salt, which forms short colourless needles closely resembling in properties the disodium salt of 2 : 2′-bis(phenarsazinic acid). The salt was washed with 90% alcohol, absolute alcohol, and ether and dried at 140—150° (Found : Na, 7·5. $C_{26}H_{20}O_4N_2As_2Na_2$ requires Na, 7·4%). When a warm aqueous solution of the disodium salt was acidified with dilute

hydrochloric acid, 2 : 2'-*bis*(8-*methylphenarsazinic acid*) was precipitated as a white amorphous powder. It does not melt at 320° (Found : As, 26·0. $C_{26}H_{22}O_4N_2As_2$ requires As, 26·0%).

2 : 2'-*Bis*(10-*bromo*-8-*methyl*-5 : 10-*dihydrophenarsazine*) (formula as I; X = Me) was prepared from the preceding acid (1·0 g.), suspended in a boiling mixture of alcohol (25 c.c.) and hydrobromic acid (const. b. p.; 20 c.c.) containing a trace of iodine, as described for the preceding chloro-compound. It was a red micro-crystalline substance. For analysis it was dried at 140° (Found : Br, 22·8. $C_{26}H_{20}N_2Br_2As_2$ requires Br, 22·7%).

2 : 2'-*Bis*(10-*iodo*-8-*methyl*-5 : 10-*dihydrophenarsazine*) was prepared in a similar manner to the corresponding chloro-compound from 2 : 2'-bis(8-methylphenarsazinic acid) (1·4 g.), alcohol (25 c.c.), and hydriodic acid (approx. 30%; 20 c.c.). It was a purplish-red solid which was unmelted at 320° (Found : I, 32·9. $C_{26}H_{20}N_2I_2As_2$ requires I, 33·2%).

5 : 8-*Dichloro*-13 : 14 : 5 : 8-*tetrahydroisobenzarsazinephenarsazine* (VII).—The condensation of o-phenylenediamine (5·3 g.; 1 mol.) with *o*-bromophenylarsinic acid (27·4 g.; 2 mols.) by boiling with potassium carbonate (21·4 g.), a trace of copper powder, and amyl alcohol (100 c.c.) for 5 hours gave a very discoloured product. All attempts to purify it in the ordinary way were unsuccessful. The crude product (2·0 g.), dissolved in a boiling mixture of alcohol (20 c.c.) and hydrochloric acid (16 c.c.) containing a trace of iodine, was reduced with sulphur dioxide in the usual way and a discoloured product again resulted. Since this could not be crystallised, it (3·4 g.) was suspended in acetic acid (30 c.c.) and oxidised with hydrogen peroxide (20 vol.; 4·2 c.c.) as previously described. The insoluble product was dissolved in hot dilute aqueous sodium hydroxide, the solution filtered, and the filtrate acidified. The precipitated acid was reduced again as just described. The precipitated *chloro-compound* was dark brown, insoluble in all the usual solvents, and remained unmelted at 320° (Found: Cl, 15·15. $C_{18}H_{12}N_2Cl_2As_2$ requires Cl, 14·9%).

1 : 3-*Phenylenediaminodi*-o-*phenylarsinic Acid* (V).—A mixture of *m*-phenylenediamine (m. p. 95°; 5·26 g.; 1 mol.), *o*-bromophenylarsinic acid (27·4 g.; 2 mols.), anhydrous potassium carbonate (21·4 g.), amyl alcohol (100 c.c.), and a trace of copper powder was boiled under reflux for 5 hours. The product was worked up as described for 4 : 4-bis(diphenylamine-2'-arsinic acid). The somewhat discoloured *acid* obtained (22% yield) was crystallised with difficulty from dilute acetic acid and dried at 160° (Found : As, 29·25. $C_{18}H_{18}O_6N_2As_2$ requires As, 29·5%). It is a colourless solid, unmelted at 325°, insoluble in water, sparingly soluble in

glacial acetic acid and in dilute mineral acids. Its ready solubility in a mixture of hydrochloric acid and alcohol distinguishes it from the corresponding ring acid.

12 : 14(or 8 : 14)-*Dichloro*-5 : 7 : 12 : 14(or 5 : 13 : 8 : 14)-*tetrahydrobenzarsazinephenarsazine* (VIII or IX) was prepared by reducing a boiling solution of the preceding acid (5·4 g.) in alcohol (54 c.c.) and hydrochloric acid (43 c.c.) in the usual way. The precipitated chloro-compound (69% yield) was washed with alcohol and dried at 140°. It formed clusters of slender yellow prisms (Found : As, 31·25; Cl, 14·5. $C_{18}H_{12}N_2Cl_2As_2$ requires As, 31·4; Cl, 14·9%).

When *NN'*-diphenyl-*m*-phenylenediamine (5·95 g.), arsenious chloride (9·17 g.), and *o*-dichlorobenzene (34 c.c.) were boiled for 5 hours, stout red prisms formed, which were filtered off from the hot solution, washed with hot *o*-dichlorobenzene and with benzene, and dried at 140° (yield, 7·75 g.; 71%) (Found : Cl, 15·1%).

The products of these two preparations remained unmelted at 320° but did not appear to be identical. Apart from their differences in colour and crystalline form when viewed under the microscope, the former had a more pronounced effect on the mucous membrane than the latter. The diarsinic acid obtained from each on oxidation (see below) gave on reduction a chloro-compound : that derived originally from 1 : 3-phenylenediaminodi-*o*-phenylarsinic acid had a marked tendency to crystallise and a marked effect on the mucous membrane, whereas that derived originally from *NN'*-diphenyl-*m*-phenylenediamine was amorphous and had no effect on the mucous membrane. Both substances were sufficiently soluble in acetone to impart to it a yellow colour, which was discharged on addition of an equal volume of a dilute aqueous solution of chloramine-T, a small quantity of a white substance (unmelted at 325 being precipitated.

5 : 7 : 12 : 14(or 5 : 13 : 8 : 14)-*Benzarsazinicphenarsazinic acid* wa prepared from either form of the foregoing compound by oxidatio with hydrogen peroxide in glacial acetic suspension, as describ for 2 : 2'-bis(phenarsazinic acid), the quantities being proportion The product was purified through the *disodium* salt, which form colourless soft needles, almost insoluble in cold or hot 20% aqueo sodium hydroxide and but slightly soluble in cold water. F analysis, the salt was washed with 90% alcohol, absolute alcohol, a ether and dried at 140—145° (Found : Na, 9·1. $C_{18}H_{12}O_4N_2As_2N$ requires Na, 8·9%). When first precipitated, the free *acid* w somewhat gelatinous, but it was finally obtained as a white amorph powder similar in properties to the other arsinic acids described this communication (Found : As, 31·8. $C_{18}H_{14}O_4N_2As_2$ requi

As, 31·8%). The acid also forms crystalline calcium and barium salts, both insoluble in hot and in cold water, a white gelatinous silver salt soluble in aqueous ammonia, heavy white gelatinous lead and mercuric salts, a pale yellow gelatinous mercurous salt, and a brown gelatinous ferric salt.

12 : 14(or 8 : 14)-*Dibromo*-5 : 7 : 12 : 14(or 5 : 13 : 8 : 14)-*tetrahydrobenzarsazinephenarsazine*.—A hot suspension of the preceding compound (1·0 g.) in alcohol (20 c.c.) and hydrobromic acid (const. b. p.; 16 c.c.) containing a trace of iodine was reduced in the usual way. The product was washed with a mixture of alcohol and hydrobromic acid, then with alcohol and ether, and dried at 150° (Found: Br, 27·95. $C_{18}H_{12}N_2Br_2As_2$ requires Br, 28·3%). It crystallised in deep yellow prisms and remained unmelted at 325°.

12 : 14(or 8 : 14)-*Di-iodo*-5 : 7 : 12 : 14(or 5 : 13 : 8 : 14)-*tetrahydrobenzarsazinephenarsazine*.—(*a*) This was prepared in a similar manner to the preceding dibromo-compound (Found: I, 38·1. $C_{18}H_{12}N_2I_2As_2$ requires I, 38·5%). It was a deep red, microcrystalline powder resembling the bromo- and chloro-compounds in general properties. It is somewhat interesting that when 5 : 7 : 12 : 14(or 5 : 13 : 8 : 14)-benzarsazinicphenarsazinic acid is boiled with a mixture of alcohol and concentrated hydriodic acid no reduction of the arsenic takes place.

(*b*) 5 : 7 : 12 : 14(or 5 : 13 : 8 : 14)-Benzarsazinicphenarsazinic acid (0·8 g.) was boiled with acetic acid (20 c.c.) and to the hot suspension hypophosphorous acid (*d* 1·136; 10 c.c.) was added. No reduction took place. On addition of iodine (3·3 g.) in small portions to the boiling suspension, a vigorous reaction took place and a deep red, microcrystalline powder was precipitated. This substance was formed as soon as the first trace of iodine was added and no signs of the preliminary formation of a cacodyl compound were observed. When all the iodine had been added, the liquid was treated with a further 30 c.c. of acetic acid, cooled, and filtered. The product, washed with acetic acid, alcohol, and ether and dried at 140°, appeared to be identical with that obtained as described under (*a*) (Found: I, 38·0%).

On warming the above dichloro-compound with dilute ammonia on the water-bath for an hour, the colour changed from yellow to greyish-white. The product was readily soluble in hot or cold *n*-propyl and benzyl alcohols and also in hot glacial acetic acid, thus behaving exactly like 10 : 10′-oxy-5 : 10-dihydrophenarsazine (Burton and Gibson, J., 1926, 462).

The condensation of *p*-phenylenediamine with *o*-bromophenylarsinic acid, carried out as described for *m*-phenylenediamine, gave a much discoloured product which it was found impossible to purify.

7 : 14(or 13 : 14)-*Dichloro*-5 : 12 : 7 : 14(or 5 : 8 : 13 : 14)-*tetrahydrobenzarsazinephenarsazine* (X or XI) was prepared by boiling *NN'*-diphenyl-*p*-phenylenediamine (m. p. 145°; 15·6 g.; 1 mol.), arsenious chloride (24·1 g.; 2·2 mols.), and *o*-dichlorobenzene (90 c.c.) for 5 hours under reflux. The product (yield, 49%) was worked up as in similar condensations, being finally washed with benzene and dried at 130° (Found: Cl, 14·9. $C_{18}H_{12}N_2Cl_2As_2$ requires Cl, 14·9%). It was unmelted at 320°. When it was oxidised to the arsinic acid (see below), and this reduced in the manner described for similar substances, the chloro-compound was reobtained in orange-red, doubly refracting, prismatic needles (Found: Cl, 14·6%).

5 : 12 : 7 : 14(or 5 : 8 : 13 : 14)-*Benzarsazinicphenarsazinic Acid*.—The oxidation of the preceding compound (12·2 g.) with hydrogen peroxide (20 vol.; 20 c.c.) in acetic acid (122 c.c.) suspension was carried out as described for 2 : 2'-bis(phenarsazinic acid), but the reaction took a somewhat longer time. Water (244 c.c.) was added and, after cooling, the crude acid was filtered off and purified through the *disodium* salt. On addition of 20% sodium hydroxide solution to the hot discoloured solution of the disodium salt, the latter was precipitated in large flat plates. This particular disodium salt appeared to crystallise the most easily of all the disodium salts in this series. The salt was purified by dissolving it in warm water, adding 33% sodium hydroxide solution, and allowing the salt to crystallise slowly; it was then obtained in colourless flat plates and needle-shaped crystals. The salt can also be crystallised from aqueous acetone. For analysis, it was washed with 90% alcohol and absolute alcohol and dried at 140° (Found: Na, 8·8. $C_{18}H_{12}O_4N_2As_2Na_2$ requires Na, 8·9%).

5 : 12 : 7 : 14(or 5 : 8 : 13 : 14)-*Benzarsazinicphenarsazinic acid* was precipitated by the addition of hydrochloric acid to a warm aqueous solution of the preceding sodium salt. It was recrystallised with difficulty from dilute acetic acid and obtained in colourless rhomb-shaped plates, which did not melt at 320° although slight darkening took place somewhat above 290° (Found: As, 31·6. $C_{18}H_{14}O_4N_2As_2$ requires As, 31·8%). It was sparingly soluble in hot glacial acetic acid and insoluble in water. Although the acid was slightly soluble in a mixture of alcohol and hydrochloric acid, the hydrochloride was not isolated. The salts resemble those of the isomeric acid except that the calcium salt appears to be slightly soluble in water.

7 : 14(or 13 : 14)-*Dibromo*-5 : 12 : 7 : 14(or 5 : 8 : 13 : 14)-*tetrahydrobenzarsazinephenarsazine*.—The preceding acid (0·75 g.), suspended in a hot mixture of alcohol (18 c.c.) and hydrobromic acid (38%; 15 c.c.) containing a trace of iodine, was reduced as described

for the chloro-compound. The product formed deep red, doubly refracting, prismatic needles resembling those of the chloro-compound. It was unmelted at 320° and insoluble in all the usual solvents (Found: Br, 27·9. $C_{18}H_{12}N_2Br_2As_2$ requires Br, 28·3%).

The di-iodo compound was prepared in an analogous manner or by the hypophosphorous acid reduction method but could not be purified.

We wish to thank Mr. C. M. Roberts, Assistant in the Chemistry Department, for valuable help in some of the preparative work connected with this investigation.

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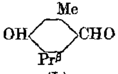
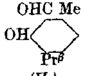
CCLXXXVIII.—*By-products of the Gattermann Aldehyde Reaction.*

By FRANK BELL and THOMAS ANDERSON HENRY.

THE Gattermann synthesis of *p*-hydroxybenzaldehydes, depending on the primary production of an aldimine by the action of hydrocyanic acid on a phenol, has been the subject of a considerable number of modifications, mainly designed to avoid the use of anhydrous hydrocyanic acid. That due to Adams and Montgomery (*J. Amer. Chem. Soc.*, 1923, **45**, 2373; 1924, **46**, 1518) has been used in these laboratories (Henry and Sharp, J., 1926, 2432), and the present paper gives an account of certain by-products isolated during the preparation of *p*-hydroxybenzaldehydes by this method.

Thymol is stated to give a quantitative yield of the corresponding *p*-aldehyde (I), but a trace of the *o*-aldehyde (II) is invariably formed, together with a small amount of *dithymylacetonitrile* (III).


(I.)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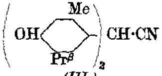
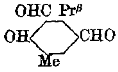
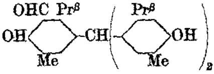

(III.)

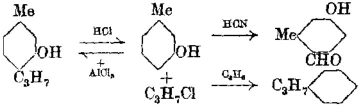
Carvacrol gives analogous products. Kobek (*Ber.*, 1883, **16**, 2104) isolated a small amount of carvacroldialdehyde (IV) when preparing

(IV.) 

 (V.)

carvacrolaldehyde by the Reimer–Tiemann process, and the formation of this dialdehyde in the Gattermann reaction is now

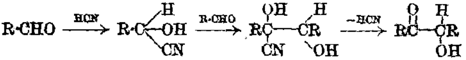
shown by the isolation of its condensation product (V) with carvacrol. In some experiments with thymol, *iso*propylbenzene and *m*-cresolaldehyde (VI) (*o*-cresolaldehyde in the case of carvacrol) were isolated, the amounts of these compounds being greatest when the yield of aldehyde was least. This result was traced to the fact that under the conditions of aldehyde formation it is possible to convert thymol almost completely into *m*-cresol and *iso*propylbenzene



(VI.)

when no hydrocyanic acid is present, thus providing a further example of the reversibility of the Friedel–Crafts synthesis (compare Jacobsen, *Ber.*, 1885, **18**, 339). The possibility of utilising this reaction to introduce the *iso*propyl group into compounds dissolved in non-reactive solvents, *e.g.*, ether, xylene, or *p*-cymene, still awaits examination. A recent paper (Berry and Reid, *J. Amer. Chem. Soc.*, 1927, **49**, 3142) describes the transfer of an *isopropyl* group from di*iso*propylbenzene into naphthalene.

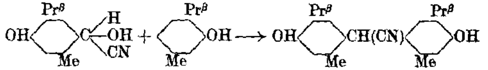
The conditions of the formation of substituted acetonitriles, such as dithymylacetonitrile (III), have been examined. It is well known that aromatic aldehydes show very varying behaviour on treatment with potassium cyanide in aqueous–alcoholic solution. One group, which includes benzaldehyde, *p*-chlorobenzaldehyde (Hantzsch and Glover, *Ber.*, 1907, **40**, 1519), and *o*-methoxybenzaldehyde (Irvine, J., 1901, **79**, 670), readily yields the corresponding benzoins, whereas *o*- and *p*-hydroxybenzaldehydes undergo resinification, and in still other cases, *e.g.*, *o*-nitrobenzaldehyde (Ekecrantz and Ahlqvist, *Ber.*, 1908, **41**, 878; 1910, **43**, 2606), a variety of products other than the benzoin is obtained. There is little doubt of the correctness of Lapworth's theory of the benzoin change (J., 1903, **83**, 995; compare Greene and Robinson, J., 1922, **121**, 2182), according to which the aldehyde, R·CHO, first adds on hydrogen cyanide, then combines with a further molecule of aldehyde, and finally eliminates hydrogen cyanide as in (*A*). It seemed possible that the cyanohydrin phase in the condensation might be detected in the case of



(*A*)

even the hydroxybenzaldehydes, if some substance were present in the solution with which the cyanohydrin might react to form a

stable product. Accordingly mixtures of hydroxybenzaldehydes with the corresponding phenols were warmed with potassium cyanide. In one case only was crystalline material isolated, thymolaldehyde and thymol giving a 12% yield of dithymylacetonitrile.



It might be anticipated that the yield of the nitrile would be considerably increased if the potassium cyanide were replaced by hydrogen cyanide. With this end in view hydrogen chloride was passed into a dry benzene solution of, *e.g.*, thymolaldehyde and thymol containing zinc cyanide in suspension. Only derivatives of triphenylmethane were obtained, and this result is interpreted as indicating that cyanohydrins are not formed under these experimental conditions. The readiness of condensation suggests that the hydrogen chloride forms an intermediate addition product with the aldehyde as shown in (*B*). If, however, an alcoholic

$$R{\cdot}CHO \longrightarrow R{\cdot}CH\begin{cases}OH\\Cl\end{cases} \xrightarrow{HR'} R{\cdot}CH\begin{cases}OH\\R'\end{cases} \xrightarrow{HR'} R{\cdot}CH\begin{cases}R'\\R'\end{cases} + H_2O \quad (B)$$

solution of equimolecular quantities of the aldehyde and phenol is treated with hydrogen cyanide and the mixture is heated to the boiling point after the addition of zinc chloride, three types of behaviour are shown.

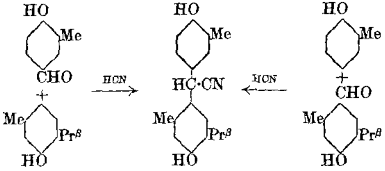
TABLE I.

(Behaviour of substituted benzaldehydes; CHO in position 1.)

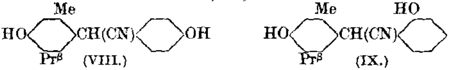
A	B	C
(produce nitriles).	(produce triphenylmethane derivatives).	(unreactive).
Me : Pr$^\beta$: OH = 2 : 5 : 4	Benzaldehyde.	NO_2 = 2
Me : Pr$^\beta$: OH = 5 : 2 : 4	Cl = 2 or 4	
Me : OH = 3 : 4	NO_2 = 3 or 4	
OH = 2 or 4	HO = 3	
OH : OH = 3 : 4		
OMe = 4		

(1) The aldehydes in column A (Table I) give the corresponding diarylacetonitriles, in some cases in quantitative yields. That it is the nuclear hydrogen atom para to the hydroxyl group in the phenol, which is involved in this condensation is clear from the fact that *o*-cresolaldehyde and thymol give the same product (VII) as thymolaldehyde and *o*-cresol. Even when the *o*- and *p*-positions are both equally accessible, as in phenol, condensation takes place

almost exclusively in the *p*-position, the product then formed being (VIII), and the isomeride (IX) could not be detected.



(VII.)



(VIII.) (IX.)

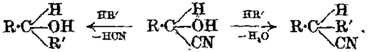
(2) On the other hand, benzaldehyde itself and its derivatives shown in column *B* (Table I) give triphenylmethane derivatives, and since the yield of these substances greatly exceeds that obtained when hydrogen cyanide is absent, it seems likely that reaction (II) is in operation in place of, or in addition to, reaction (I) :—

$$\text{(I) R·CHO} + \text{HR}'\text{·OH} \longrightarrow \text{R·CH(OH)·R}'\text{·OH} \xrightarrow{\text{HR}'\text{·OH}} \text{R·CH(R}'\text{·OH)}_2 + \text{H}_2\text{O}.$$

$$\text{(II) R·CH(OH)·CN} + \text{HR}'\text{·OH} \xrightarrow[-\text{HCN}]{} \uparrow$$

o-Nitrobenzaldehyde is unique in so far as it is isolated from the reaction mixture in the form of its cyanohydrin, which is apparently very unreactive.

This variety of results is all the more remarkable since mandelic acid and mandelonitrile condense normally with a whole series of phenols (Bistrzycki and Flatau, *Ber.*, 1895, **28**, 989; 1897, **30** 124; Bistrzycki and Simonis, *Ber.*, 1898, **31**, 2812; Cramer, *ibid.* p. 2813; Simonis, *ibid.*, p. 2821). Considerable further investig ation is required to determine the influence of (*a*) substituents and (*b* physical conditions, *e.g.*, acidity of the solution, on the relativ reactivity of the hydroxyl and cyano-groups of cyanohydrins. W have little doubt that the triphenylmethane formation indicate cyano-group reactivity, the intermediate diphenylmethane derivativ undergoing further condensation under the experimental condition whereas nitrile formation indicates hydroxyl group reactivity (*C*



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The fact that the substituted nitriles do not undergo further co

densation to triphenylmethane derivatives is only in line with the diminished reactivity of the cyano-group which is shown by its resistance to hydrolytic agents. It appears that the hydroxyl group by virtue of its lone pairs of electrons is a more ready electron source than the cyano-group and that when the nucleus of a cyanohydrin has a positive character the hydroxyl group will tend to become, relative to the cyano-group, less negative, and at the same time less reactive.

Experimental.

Thymolaldehydes and By-products.—Into an ice-cold, well-stirred mixture of thymol (50 g.), zinc cyanide (100 g.), and benzene (200 c.c.; distilled from phosphoric oxide), was passed a rapid stream of dry hydrogen chloride until it ceased to be absorbed. Aluminium chloride (75 g.) was then added and the stirring continued for 4 hours in a slow current of hydrogen chloride. Towards the end, the reaction bottle was kept immersed in water at about 50°. The semi-solid product was transferred into 10% hydrochloric acid and distilled in steam until thymolaldehyde appeared in the condenser. The residue left on the removal of the solvent from the benzene layer of the steam distillate was distilled in three fractions; the residue in the flask then set solid and proved to be *p*-thymolaldehyde (I). The first fraction, b. p. 60—80°/15 mm., consists mainly of *iso*propylbenzene and is occasionally negligible in amount (see below). The second (b. p. 100—110°/15 mm.) and third (b. p. 110—120°/15 mm.) fractions were dissolved in alcohol and treated with aqueous-alcoholic semicarbazide solution. The precipitate immediately given with fraction 2, after repeated extraction with boiling alcohol, formed a white powder, m. p. 262° (decomp.), which was identified as *m*-cresolaldehyde semicarbazone (Found: C, 55·1; H, 5·6; N, 21·3. Calc.: C, 56·0; H, 5·7; N, 21·8%) by hydrolysis in the following manner: A mixture of the substance (3 g.), sulphuric acid (10 c.c.), and water (50 c.c.) was heated to boiling and the resultant *m*-cresolaldehyde (VI) removed in a current of steam. It crystallised from petroleum in long needles, m. p. 63° (Found: C, 70·4, 70·3; H, 5·8, 6·0. Calc.: C, 70·6; H, 5·9%).

In the case of fraction 3 acicular crystals gradually separated and after repeated crystallisation from alcohol had m. p. 198° (Found: C, 61·5; H, 7·2; Sem., 31·4%). The semicarbazide group (Sem. = N·NH·CO·NH_2) was estimated by the method of Veibel (*Bull. Soc. chim.*, 1927, **41**, 1410). This compound can only be the *semicarbazone* of 2-aldehydo-3-methyl-6-*iso*propylphenol (*o*-thymolaldehyde) (II) ($C_{12}H_{17}O_2N_3$ requires C, 61·3; H, 7·2; Sem., 31·1%).

The residue left after steam distillation was extracted with ether, and the extract evaporated. Two methods of purifying the crude

p-aldehyde (about 50 g.; identical with the yield obtained by Gattermann's original method, *Ber.*, 1898, **31**, 1765) were adopted: (1) extraction with 25% alcohol, a small crystalline residue, m. p. 205°, being finally obtained; (2) crystallisation from alcohol, the final low-melting crops being dissolved in chloroform and filtered from a small amount of the same substance, m. p. 205°, subsequently shown to be dithymylacetonitrile (see p. 2224). 4-Aldehydo-3-methyl-6-*iso*propylphenol (I) forms colourless needles, m. p. 135°; when aqueous-alcoholic semicarbazide solution is added to its alcoholic solution the slightly impure *semicarbazone* separates in deep yellow needles, m. p. 222° (Found: C, 60·6, 60·7; H, 7·3, 7·3%), which rapidly become colourless on recrystallisation from acetic acid or alcohol and melt at 226° (Found: C, 61·2; H, 7·3; Sem., 30·5. $C_{12}H_{17}O_2N_3$ requires C, 61·3; H, 7·2; Sem., 31·1%).

Attempts to convert *p*-thymolaldehyde into the corresponding dialdehyde by (*a*) the Adams and Montgomery method, (*b*) the Gattermann method were unsuccessful. This failure is not surprising in view of the highly substituted character of the ring, and also of the disinclination of hydrogen cyanide to attack the position ortho to a hydroxyl group. It may be mentioned that even *p*-cresol gives a very small yield of the aldehyde when submitted to the same treatment as produces a satisfactory yield from *o*-cresol (see below).

Action of Aluminium Chloride on Thymol.—As it was surmised that the formation of *iso*propylbenzene in the reaction just described was due to interaction of thymol and benzene in presence of aluminium chloride, a well-stirred mixture of thymol (25 g.), dry benzene (200 c.c.), and aluminium chloride (35 g.) was warmed at about 50° for 4 hours while a current of dry hydrogen chloride was passed in. The clear solution was poured into 10% hydrochloric acid and distilled in steam. The benzene layer of the steam distillate was separated and evaporated and the residue obtained was distilled in a vacuum, giving fractions b. p. 60°, 95—100°, 100—118°, and *ca.* 170°/15 mm. The low-boiling fraction (about 10 g.) was redistilled under ordinary pressure, and the fraction, b. p. 150—155°, redistilled from sodium. It then boiled constantly at 153° and agreed in properties with *iso*propylbenzene (Found: C, 90·3; H, 9·9. Calc.: C, 90·0; H, 10·0%). The fraction, b. p. 95—100°/15 mm., gave pure *m*-cresol, b. p. 200—202° (6 g.), which was identified as its *p*-nitrobenzoyl derivative. The higher-boiling fraction consisted of neutral substances, being apparently a mixture of *m*-tolyl ether and thymyl ether. When the above reaction was carried out in the presence of toluene a fraction, b. p. 65—75°/15 mm., was obtained which on redistillation had b. p. 175—180°, being slightly impure *p*-cymene.

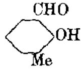
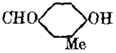
Carvacrolaldehydes and By-products.—The preparation was effected as described for thymolaldehyde (see above). The steam distillate gave fractions, b. p. 60°, 100—110°, 110—120°, and 120—130°/15 mm., and a residue of the *p*-aldehyde, which could be sublimed at 150°/1 mm. The first fraction consisted of *iso*propylbenzene (see below). The remaining fractions were dissolved separately in alcohol and treated with aqueous-alcoholic semicarbazide solution. The fraction, b. p. 100—110°/15 mm., gave crude *o*-cresolaldehyde semicarbazone (compare thymol above), and from the fraction, b. p. 110—120°/15 mm., was isolated a trace of material which crystallised from pyridine or acetic acid in thick, pale yellow prisms, m. p. 275° (Found: C, 73·2; H, 7·9; N, 7·8%). It is suggested that this compound is the *semicarbazone* of 4-hydroxy-3-aldehydo-5-methyl-2-*iso*propylphenyldicarvacrylmethane (V) ($C_{33}H_{43}O_4N_3$ requires C, 72·7; H, 7·9; N, 7·7%) formed by the interaction of carvacrol and carvacroldialdehyde during the distillation. The fourth fraction, b. p. 120—130°/15 mm., gave more soluble material, which crystallised from aqueous alcohol in long glistening needles, m. p. 180° (Found: C, 61·3; H, 7·3; Sem., 31·5%), and must be the *semicarbazone* of 2-aldehydo-6-methyl-3-*iso*propylphenol (*o*-carvacrolaldehyde semicarbazone) ($C_{12}H_{17}O_2N_3$ requires C, 61·3; H, 7·2; Sem., 31·1%).

The ether-soluble portion of the residue left after steam distillation was repeatedly extracted by decantation with petroleum (b. p. 90—120°), which slowly removed the *p*-carvacrolaldehyde (30—40 g.) as colourless plates, m. p. 102°. With aqueous-alcoholic semicarbazide solution this yielded a slightly impure, deep yellow *semicarbazone*, m. p. 222° (Found: C, 60·8; H, 7·3%), which on crystallisation from acetic acid gave colourless needles, m. p. 224° (Found: Sem., 31·1. $C_{12}H_{17}O_2N_3$ requires C, 61·3; H, 7·2; Sem., 31·1%). The tar which remained after the complete removal of this aldehyde was moistened with alcohol and kept for several weeks. Crystals slowly formed, which after recrystallisation from aqueous alcohol had m. p. 240° and were subsequently shown to consist of dicarvacrylacetonitrile (see p. 2223).

Action of Aluminium Chloride on Carvacrol (compare corresponding experiment with thymol, p. 2220).—Fractions, b. p. 60° (11 g.), 100° (11 g.), and 102—115°/15 mm. (5 g.) were obtained. The residue, after being heated to 150°/1 mm., crystallised from petroleum in long thick needles, m. p. 148—150° (0·3 g.) (Found: C, 83·3, 83·7; H, 8·5, 8·8%). This substance was not obtained in sufficient quantity for identification. The low-boiling fraction was almost pure *iso*propylbenzene, and the intermediate fraction gave *o*-cresol, b. p. 188—190° (7 g.), identified as the *p*-nitrobenzoate.

Reimer–Tiemann Reaction with Carvacrol.—Carvacrol (20 g.), sodium hydroxide (40 g.), water (300 c.c.), and chloroform (25 g.) were used. The reaction mixture was acidified and distilled in steam. The distillate consisted of unchanged carvacrol and the *o*-aldehyde, isolated only as its semicarbazone (see above). The residue was purified as described above and gave a very small yield of the *p*-aldehyde, identical with that described above.

o-*Cresolaldehydes.*—Preparation as above, *o*-cresol (50 g.) being used in place of thymol. The steam distillate, freed from solvent, boiled at 85—90°/15 mm. (15 g.), leaving only a small residue of the *p*-aldehyde. To a solution of the fraction, b. p. 85—90°/15 mm., in alcohol (15 c.c.) was added aqueous-alcoholic semicarbazide solution. The resultant precipitate (3 g.) was repeatedly extracted with boiling alcohol; the residue then remained unchanged in m. p. (248°, decomp.) by crystallisation from pyridine, from which it separated in glistening needles. It was identified as the *semicarbazone* of 6-aldehydo-2-methylphenol (X) (Found: C, 55·5;

(X.)   (XI.)

H, 5·8; N, 21·6; Sem., 38·5. $C_9H_{11}O_2N_3$ requires C, 56·0; H, 5·7; N, 21·8; Sem., 37·8%), by hydrolysis to the corresponding aldehyde, which was then converted into the known phenylhydrazone.

The ether-soluble portion of the residue left after steam distillation was extracted with boiling water until all the *p*-aldehyde (XI) about 20 g.) had been removed, leaving an uncrystallisable tar. The *p*-aldehyde gave a *semicarbazone* crystallising from acetic acid n needles, m. p. 216° (Found: N, 21·8; Sem., 37·2. $C_9H_{11}O_2N_3$ requires N, 21·8; Sem., 37·8%).

Action of Potassium Cyanide on Hydroxybenzaldehydes.—(1) No crystalline material could be isolated from the gums obtained by the action of potassium cyanide on alcoholic solutions of salicylaldehyde, *p*-hydroxybenzaldehyde, or carvacrolaldehyde, either alone or when mixed with phenol or carvacrol respectively.

(2) Nine mixtures of thymolaldehyde, alone and with thymol, potassium cyanide and aqueous alcohol were heated under reflux or varying periods. In only one experiment (*a*) in which thymo was omitted was any yield of substance, m. p. 205°, obtained, anc experiment (*b*) furnished the highest yield of the series.

(*a*) Thymolaldehyde (3·6 g.), alcohol (6 c.c.), potassium cyanid 1 g.), and water (2 c.c.) were mixed and heated at 100° for 1 houı after 2 days the mixture was made acid and left for 10 days. Th resultant tar was filtered off, and the residual solid crystallised fror

alcohol. Yield, 0·25 g.; m. p. 205°. As this experiment could not be repeated, it is assumed that the thymolaldehyde used in the first instance must have contained thymol.

(*b*) Thymolaldehyde (18 g.), alcohol (60 c.c.), thymol (12 g.), potassium cyanide (6 g.), and water (12 c.c.) were mixed and heated at 100° for 20 hours. After 2 days concentrated hydrochloric acid (10 c.c.) was added, and after 2 days more the mixture was poured into water and extracted with ether. The ethereal extract was evaporated, and the dried residue extracted with hot chloroform. The insoluble matter (4·0 g.) had m. p. 205° (see below).

Thymolaldehyde and benzonitrile underwent no interaction when a concentrated alcoholic solution was boiled under reflux or allowed to stand for some days. In the hope of obtaining the compounds in better yields, the following experiments were tried. (1) Thymolaldehyde (10 g.), thymol (20 g.), zinc cyanide (20 g.), and dry benzene (200 c.c.) were well stirred while a slow stream of dry hydrogen chloride was passed in. The mixture was maintained at 40—60° for the last 2 hours. The highly coloured, viscous mass was transferred into 10% hydrochloric acid by the aid of a small bulk of boiling alcohol, and then distilled in steam. The tarry residue was extracted with ether, the extract evaporated, and the dried mass boiled with chloroform. The colourless residue (15 g., m. p. 276°) after crystallisation from aqueous alcohol formed prisms, m. p. 280° (Found: C, 80·2; H, 8·6%). This substance must be *trithymylmethane* ($C_{31}H_{40}O_3$ requires C, 80·8; H, 8·7%), a conclusion which was confirmed by the preparation of the acetyl derivative. The compound (2·5 g.) and acetic anhydride (15 c.c.) were heated under reflux for 2 hours. On cooling, the liquid filled with crystals of *triacetylthymylmethane*, which after recrystallisation from benzene–petroleum formed glistening leaflets, m. p. 186° (Found: Ac, 22·0. $C_{37}H_{46}O_6$ requires Ac, 22·0%).

(2) Carvacrolaldehyde (10 g.) and carvacrol (25 c.c.), treated as in (1), gave *tricarvacrylmethane*, m. p. 275° (Found: C, 80·8; H, 8·8%). The compound was acetylated as described above and yielded *triacetylcarvacrylmethane*, which after crystallisation from petroleum formed leaflets, m. p. 185° (Found: C, 76·1; H, 8·1. $C_{37}H_{46}O_6$ requires C, 75·8; H, 7·9%). Both compounds gave the customary large depression in melting point when mixed with the corresponding derivatives of thymol.

Little condensation occurs if the zinc cyanide is omitted in these experiments. Moreover the yield of triphenylmethane derivatives is considerably greater than when the experiment is conducted in alcoholic solution with hydrogen chloride or zinc chloride as condensing agent.

Action of Hydrogen Cyanide on Substituted Benzaldehydes.—General method. Dry hydrogen cyanide from potassium ferrocyanide (70 g.; method of Johnson and Lane, *J. Amer. Chem. Soc.*, 1921, **43**, 357) was passed into a solution of equimolecular proportions of the aldehyde (10 g.) and the phenol in absolute alcohol (50—100 c.c.). Zinc chloride (20—25 g.) was then added, the mixture boiled for 2 hours, and the solution poured into 10% hydrochloric acid. Excess of the reagents was removed in a current of steam, and the residual solid or plastic mass filtered off.

(1) Thymolaldehyde and thymol combined to give a quantitative yield of *dithymylacetonitrile*, which after recrystallisation from alcohol formed prismatic needles, m. p. 205° (Found: C, 78·4; 78·5; H, 8·2, 8·1; N, 4·3, 4·2. $C_{22}H_{27}O_2N$ requires C, 78·3; H, 8·0; N, 4·1%). No combination occurred when the zinc chloride was omitted.

Dithymylacetonitrile was not attacked by boiling hydrochloric acid or by sulphuric acid (50—65%), and higher concentrations produced resinous masses (compare Michael and Jeanprêtre, *Ber.* 1892, **25**, 1615). Hydrolytic experiments with 3% hydrogen peroxide (Radziszewski, *Ber.*, 1885, **18**, 355) or 100% phosphoric acid (Berger and Olivier, *Rec. trav. chim.*, 1927, **46**, 600) were also unsuccessful. The substance (5 g.) was heated at 100° with potassium hydroxide (20 g.) in 90% alcohol (100 c.c.) for 10 hours. After standing 2 days, the solution was poured into 10% hydrochloric acid and the precipitated *dithymylacetamide* crystallised from alcohol. It formed a colourless, heavy crystalline powder, m. p. 243° (decomp.) (Found: C, 73·8; H, 8·2. $C_{22}H_{29}O_3N$ requires C, 74·4; H, 8·2%). *Diacetyldithymylacetonitrile*, formed by heating dithymylacetonitrile (3 g.) with acetic anhydride (15 c.c.) and recrystallising the product from chloroform–petroleum, formed needles, m. p. 174° (Found: C, 74·3, 74·1; H, 7·5, 7·5; Ac, 20·4. $C_{26}H_{31}O_4N$ requires C, 74·[illegible] H, 7·4; Ac, 20·4%). On hydrolysis with dilute alcoholic potassium hydroxide it regenerated dithymylacetonitrile, m. p. 205°.

(2) Carvacrolaldehyde and carvacrol, treated in like manner, gave a quantitative yield of *dicarvacrylacetonitrile*, which crystallised from aqueous alcohol in prisms, m. p. 240° (Found: C, 78·3; H, [illegible] N, 3·7. $C_{22}H_{27}O_2N$ requires C, 78·3; H, 8·0; N, 4·1%). [illegible]*acetylcarvacrylacetonitrile* crystallised from alcohol in colourless needles, m. p. 196° (Found: C, 74·0; H, 7·6; N, 3·5. $C_{26}H_{31}$[illegible] requires C, 74·1; H, 7·4; N, 3·3%).

(3) Thymolaldehyde and carvacrol, or carvacrolaldehyde [illegible] thymol, gave *thymylcarvacrylacetonitrile*, which formed pri[illegible] m. p. 227°, from alcohol (Found: C, 78·1; H, 8·3. $C_{22}H_{27}$[illegible] requires C, 78·3; H, 8·0%). It yielded a *diacetyl* derivative, [illegible]

145° (Found: C, 73·7; H, 7·4. $C_{26}H_{31}O_4N$ requires C, 74·1; H, 7·4%).

(4) *o*-Cresolaldehyde and thymol, or thymolaldehyde and *o*-cresol, gave *tolylthymylacetonitrile* (VII), the first pair giving a quantitative and the second a 70% yield. It crystallised from aqueous alcohol in prisms, m. p. 153° (loss in weight on drying at 100° = 10·4%) (Found for dry substance: C, 77·1; H, 7·3. $C_{19}H_{21}O_2N$ requires C, 77·3, H, 7·1%). The substance (5 g.) was warmed with potassium hydroxide (20 g.) in 90% alcohol (100 c.c.) at 100° for 24 hours. The solution was poured into 10% hydrochloric acid and extracted with ether. The ethereal extract was shaken with dilute sodium carbonate solution, and the aqueous and ethereal layers were separated and well washed with ether and water respectively. The ethereal layer was evaporated, and the dried residue extracted with hot benzene. The residual *tolylthymylacetamide* crystallised from alcohol in prisms, m. p. 211° (Found: C, 72·6; H, 7·4; N, 4·7. $C_{19}H_{23}O_3N$ requires C, 72·9; H, 7·3; N, 4·5%). The aqueous layer was poured into 10% hydrochloric acid, and the resulting gum dried in a vacuous desiccator. After boiling with benzene, it formed a pale brown powder, m. p. 188°. It was free from nitrogen and must be crude *tolylthymylacetic acid* (Found: C, 71·2, 71·6, 71·2; H, 7·1, 7·2, 6·9. $C_{19}H_{22}O_4$ requires C, 72·6; H, 7·0%). *Acetyltolylacetylthymylacetonitrile* forms prisms, m. p. 131° (Found: Ac, 23·3. $C_{23}H_{25}O_4N$ requires Ac, 22·7%).

(5) *p*-Hydroxybenzaldehyde and thymol gave a brown resinous mass, which crystallised from chloroform in needles, m. p. 142°. Recrystallised from benzene, p-*hydroxyphenylthymylacetonitrile* (VIII) formed large prisms, which on drying at 110° lost 12·6% by weight and left a residue, m. p. 144° (Found: C, 76·3; H, 6·8. $C_{18}H_{19}O_2N$ requires C, 76·8; H, 6·8%). Phenol and thymolaldehyde gave an 80% yield of the same substance.

(6) Anisaldehyde (*p*-methoxybenzaldehyde) and thymol gave a thick oil, which was extracted with ether. The gum remaining after evaporation of the ether was dissolved in chloroform. After some days crystals separated, which were well washed with petroleum and repeatedly recrystallised from benzene, pure *anisylthymylacetonitrile* being obtained in 10% yield. It formed large prisms, m. p. 106° (Found: C, 77·6; H, 7·2. $C_{19}H_{21}O_2N$ requires C, 77·3; H, 7·1%).

(7) Salicylaldehyde and thymol gave a resin, which crystallised from chloroform in prisms, m. p. 142°, and when dried at 110° lost 18·9% by weight (Found, for dry substance: C, 76·6; H, 6·9. $C_{18}H_{19}O_2N$ requires C, 76·8; H, 6·8%). The yield of purified o-*hydroxyphenylthymylacetonitrile* (IX) was less than 50% of the theoretical.

(8) Protocatechualdehyde and thymol gave a gummy mass, hich was extracted with benzene, and the product repeatedly ystallised from chloroform. *Catechylthymylacetonitrile* formed risms, m. p. 147—149° (Found: N, 4·7. $C_{18}H_{19}O_3N$ requires [, 4·7%).

(9) Benzaldehyde and thymol gave a quantitative yield of henyldithymylmethane, which crystallised in prisms, m. p. 167—68°, containing one molecule of alcohol (loss in weight at 110° = 0·5%; calc., 11%). This description agrees with that of Russanow Ber., 1889, **22**, 1947).

(10) *m*-Hydroxybenzaldehyde and thymol gave a poor yield of n-*hydroxyphenyldithymylmethane*, which crystallised from chloroform n prisms, m. p. 165° (Found: C, 80·5; H, 8·1. $C_{27}H_{32}O_3$ requires C, 80·2, H, 7·9%).

(11) *o*-Nitrobenzaldehyde and thymol gave a product, which crystallised from chloroform in needles, m. p. 95—97°, and proved to be o-nitrobenzaldehydecyanohydrin (Found: C, 54·1; H, 3·5. Calc.: C, 53·9%; H, 3·4%). The fact that this cyanohydrin survives the general method of treatment (see above) is remarkable. No different result was obtained when phenol was used in place of thymol.

(12) *m*-Nitrobenzaldehyde and thymol gave an almost quantitative yield of m-*nitrophenyldithymylmethane*, which crystallised readily from aqueous alcohol in prisms, m. p. 171° (Found: C, 74·7; H, 7·2. $C_{27}H_{31}O_4N$ requires C, 74·8; H, 7·2%).

(13) *p*-Nitrobenzaldehyde and thymol gave a tarry mass; this after several recrystallisations from benzene formed colourless needles, which became pale yellow on drying and then melted at 145° (loss in weight on drying, 20·9. $C_{27}H_{31}O_4N,1\frac{1}{2}C_6H_6$ requires loss, 21·2%) (Found for the residual p-*nitrophenyldithymylmethane*: C, 75·0; H, 7·2. $C_{27}H_{31}O_4N$ requires C, 74·8; H, 7·2%). The mother-liquor contained *p*-nitrobenzaldehydecyanohydrin.

(14) *p*-Chlorobenzaldehyde and thymol gave a quantitative yield of p-*chlorophenyldithymylmethane*, which crystallised from alcohol in prisms; these, dried at 110°, lost 15·0% by weight, and the residue melted at 156° (Found: C, 76·4; H, 7·3. $C_{27}H_{31}O_2Cl$ requires C, 76·7; H, 7·3%).

(15) *o*-Chlorobenzaldehyde and thymol gave a viscid mass, which, however, readily crystallised from aqueous alcohol to give an almost theoretical yield of o-*chlorophenyldithymylmethane*. Dried at 110°, this lost 16·6% by weight, and the residue melted at 138° (Found: C, 76·4; H, 7·2. $C_{27}H_{31}O_2Cl$ requires C, 76·7; H, 7·3%).

Since it might be suggested that when triphenylmethane formation occurs, combination takes place between the aldehyde and the

phenol before the hydrogen cyanide is introduced, the experiments with *m*-nitro- and *o*- and *p*-chloro-benzaldehydes were repeated, the thymol not being added until after the passage of the hydrogen cyanide. The experimental results were unaltered, and this is not surprising in face of the results of the following experiments.

(*a*) The experiment with *p*-chlorobenzaldehyde (14 above) was repeated, this time without the addition of zinc chloride. No combination occurred.

(*b*) *p*-Chlorobenzaldehyde (5 g.), thymol (10·7 g.), and zinc chloride (20 g.) in absolute alcohol (40 c.c.) were heated under reflux for 4 hours and then poured into 10% hydrochloric acid and the excess of the reagents was removed in steam. The residual crude *p*-chlorophenyldithymylmethane weighed 4 g. (25% yield).

(*c*) *m*-Nitrobenzaldehyde and thymol treated as in (*b*) gave crude *m*-nitrodithymylmethane in only 20% yield.

The authors desire to express their thanks for assistance in the experimental work to the late Mr. S. E. Pusey and to Mr. H. C. Clarke.

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CCLXXXIX.—*Polyiodide Equilibrium in Aqueous and Salt Solutions.*

By JOHN STANLEY CARTER.

THERE is abundant evidence to show that the dissolution of iodine in solutions of iodides involves the formation of polyiodides, and that in dilute solutions the whole of the combined iodine is present as tri-iodide. Consequently, saturation of dilute solutions of iodides with iodine involves the establishment of the equilibrium $I' + I_2 \rightleftharpoons I_3'$. When active masses are identified with actual concentrations the equilibrium expression is $K = [I'] \times [I_2]/[I_3']$. If the solutions are dilute, the concentration of free iodine may be assumed to be constant and equal to the solubility in the pure solvent.

The measurements now recorded have reference to the solubility of iodine at 25° in solutions of sodium iodide, the concentrations of which were varied between fairly wide limits, (*a*) pure water and (*b*) a $1{\cdot}698M_w$-sodium sulphate solution being used as solvents. The relevant data are in Tables I and II, all concentrations being expressed as mols. per 1000 g. of water, since this mode of expression has already been found satisfactory in correlating solubility measurements in aqueous and concentrated salt solutions (*J.*, 1925, **127**,

2861). The solubility data have been utilised on the assumption that the only polyiodide present is the tri-iodide, and that the iodide and the tri-iodide have no influence on the solubility of iodine as such. The concentration of tri-iodide is then given by the difference between the observed solubility s and the solubility s_0 in the iodide-free solvent. The concentration of uncombined iodide is the difference between the initial concentration of iodide c and that of the tri-iodide. The last column gives the values of K. Iodide and polyiodide are assumed to be completely ionised ir both media.

TABLE I.

Solvent, water; $s_0 = 1{\cdot}324 \times 10^{-3}$.

$c \times 10^3$.	$s \times 10^3$.	$K \times 10^3$.	$c \times 10^3$.	$s \times 10^3$.	$K \times 10^3$.
0·392	1·494	1·7	47·20	24·66	1·353
0·7838	1·676	1·63	97·88	50·04	1·336
1·959	2·260	1·447	221·9	116·1	1·235
3·918	3·199	1·442	358·0	192·9	1·150
7·838	5·126	1·403	604·4	349·1	0·977
19·59	10·96	1·366	1135	757·5	0·664

TABLE II.

Solvent, 1·698M_w-sodium sulphate; $s_0 = 3{\cdot}784 \times 10^{-4}$.

$c \times 10^3$.	$s \times 10^3$.	$K \times 10^3$.	$c \times 10^3$.	$s \times 10^3$.	$K \times 10^3$.
0·251	0·413	2·2	52·77	11·97	1·346
0·655	0·497	1·71	65·34	14·79	1·325
1·431	0·666	1·502	66·22	15·13	1·321
3·271	1·048	1·472	100·6	23·17	1·293
6·531	1·738	1·439	154·2	37·79	1·181
12·74	3·063	1·416	207·8	53·59	1·097
26·19	6·031	1·375	347·7	101·6	0·919
52·53	11·90	1·347	572·9	203·5	0·689

A consideration of the data shows that the value of K is ı constant, the variation being such as to indicate that the tender to form higher polyiodides (*e.g.*, pentaiodide) increases w increasing initial concentration of iodide. The value of K for ı two series follows the same course, but changes relatively v slowly between $c = 0{\cdot}002$ and 0·I. It is in this region that results are most suitable for correlating the two series of meası ments, since in these dilute solutions practically the whole of combined iodine may be assumed to be present as tri-iodide, K should be constant. Actual constancy is, of course, not obser but the magnitude of K is approximately the same in both se and the drift in the value is small. In view of the nature of assumptions involved, this approximate agreement with the requ ments of the mass-law equation is not unsatisfactory and sup the view that the relation between active masses and actual centrations is much closer than would be anticipated from

siderations of the theory of activities. The value of the ratio $[I']/[I_3']$ is about 1·05 for the sulphate-free solutions and about 3·5 for the sulphate solutions. Apart from the fact that it indicates that the extent of polyiodide formation is greatly depressed in presence of sulphate, the difference between these values is also of interest from the point of view of the theory of activities. Although, in the absence of values for the activity coefficients concerned, it is impossible to make a quantitative prediction, a consideration of the ideas associated with the theory of activities leads to the conclusion that within this concentration range the value of this ratio should be practically independent of the presence of added salts.

Results in extremely dilute solutions are considerably influenced by small errors in the actual determination of the dissolved iodine, but it is considered that the observed effects are real.

Jakowkin (*Z. physikal. Chem.*, 1896, **20**, 19), Dawson (J., 1901, **79**, 238), and Pearce and Eversole (*J. Physical Chem.*, 1924, **28**, 245) have investigated the partition of iodine between solutions of iodides and an organic solvent and found that K is approximately constant for dilute solutions, but not for concentrated solutions. This is clearly shown by the data presented in Table III, which refer to the equilibria established when iodine is distributed between carbon tetrachloride and fairly concentrated solutions of sodium iodide; under C and W are recorded the concentrations of iodine (mols./1000 g. of solvent) in the carbon tetrachloride and aqueous phases, respectively, and under $[I_2]$ are tabulated the concentrations of the uncombined iodine in the aqueous layer, calculated from a knowledge of the distribution ratio. The last column contains the values of K computed on the assumption that the only polyiodide present is the tri-iodide.

The ratio in which iodine is distributed between water and carbon tetrachloride was first determined:

$C \times 10^3$ (approx.) ...	57	46	25	21	10
Partition ratio	54·8	54·2	53·5	53·6	53·2
				53·5 (mean of last three)	

A curve was then drawn from the data, the assumption being made that neither the iodide nor the polyiodide has any influence on the value of the distribution ratio: as the salting-out effect of the iodide ion is practically nil, this assumption is not unreasonable.

The values of K apparently tend towards constancy when the concentration of iodine is small. The data indicate the presence of polyiodides more complex than the tri-iodide in the more concentrated solutions.

TABLE III.

Sodium iodide = $0\cdot9940M_w$.				Sodium iodide = $0\cdot4933M_w$.			
$C \times 10^3$.	$W \times 10^2$.	$[I_2] \times 10^5$.	$K \times 10^3$.	$C \times 10^3$.	$W \times 10^2$.	$[I_2] \times 10^5$.	$K \times 10^3$.
0·356	0·444	0·665	1·49	0·663	0·414	1·240	1·47
0·840	1·047	1·570	1·478	3·684	2·258	6·885	1·440
1·875	2·331	3·503	1·462	8·083	4·853	15·13	1·390
3·510	4·318	6·533	1·440	9·067	5·430	16·94	1·375
3·502	4·452	6·713	1·434	20·39	11·31	38·12	1·287
7·236	8·872	13·52	1·382	36·42	17·34	67·82	1·259
16·86	20·12	31·56	1·247	47·42	21·24	87·50	1·168
21·61	25·81	40·41	1·154	49·82	21·99	91·75	1·150
33·05	36·56	61·39	1·055				
53·08	51·36	97·23	0·913				

Experimental.—Iodine, sodium sulphate, and carbon tetrachloride were purified by customary methods. The sodium iodide contained no impurity other than water. The usual precautions were taken in determining solubilities and distribution ratios.

My thanks are due to Professor H. M. Dawson for suggesting these experiments and for his criticism and advice.

UNIVERSITY OF LEEDS. [*Received, June 12th, 1928.*]

CCXC.—*The Laws of Aromatic Substitution. Part IX.*

By BERNHARD FLÜRSCHEIM and ERIC LEIGHTON HOLMES.

IN Part VIII (this vol., p. 1607), the *o*-, *p*-, and *m*-percentages produced by nitration of the complete series $C_6H_5{\cdot}C(R_1)(R_2)(R_3)$ (R_1 and R_2 = Cl,CO_2Et,H; R_3 = Cl,CO_2Et) have been accurately determined. The results have shown that a polar effect, which had long been recognised by one of us where *o*-substitution is concerned and had been postulated by Robinson also for the *m*- and *p*-positions, actually exists, and may be very pronounced, in *all positions. At the same time, an alternating effect (quantitative* factor "*q*"), as postulated by one of us (*e.g.*, $C_6H_5\cdots C{-}Cl$ and $C_6H_5{-}C\cdots CO_2Et$), has been found to be superposed on the polar effect, tending in the above series to reverse the relative order in which the substituents would cause *m*-substitution if their polar effects were the only factor.

The present investigation has been extended to compounds wherein R_1 or R_1 and R_2 = CN and covers the following series :

$C_6H_5{\cdot}CH_2{\cdot}CN$;

$C_6H_5{\cdot}CHCl{\cdot}CN$, $C_6H_5{\cdot}CH(CO_2Et){\cdot}CN$, $C_6H_5{\cdot}CH(CN)_2$, $C_6H_5{\cdot}CH(OH){\cdot}CN$;

$C_6H_5{\cdot}C(CO_2Et)_2{\cdot}CN$, $C_6H_5{\cdot}C(CO_2Et)(CN)_2$;

also $C_6H_5{\cdot}CN$ and *m*-$NO_2{\cdot}C_6H_4{\cdot}N{:}CH{\cdot}C_6H_5$.

The new data are to be found in Table I. For comparison, the ratios of *m*- to *o*- + *p*-substitution determined in Part VIII are recapitulated in Table II.

TABLE I.

No.	Substance.	Medium.	Nitration products, mol. %. $o + p$.	m.	Mean mol. %, m.	$\frac{m}{o+p}$ (%).
1	PhCN	HNO_3 d 1·52	12·0 11·5	88·00 88·50	88·25*	751*
2	Ph·CH_2·CN	,,	86·85 87·75	13·15 12·25	12·70†	14†
3	Ph·CH(CO_2Et)·CN	,,	62·55 63·05	37·45 36·95	37·20	59·2
4	Ph·CH$(CN)_2$	,,	31·0	69·0		
5	,,	,,	32·70	67·30	67·90	211·8
6	,,	,,	32·55	67·45		
7	Ph·C$(CO_2Et)_2$·CN	,,	29·85 31·00	70·15 69·00	69·55	228·6
8	Ph·C(CO_2Et)$(CN)_2$	,,	12·10 12·95	87·90 87·05	87·5	698·4
9	Ph·CHCl·CN	,,	46·20	53·80	50·05‡	100·20‡
10	,,	,,	49·95	50·05		
11	Ph·CH(OH)·CN	,,	56·15 56·70	43·85 43·30	43·55	77·25
12	Ph·CH:N·C_6H_4·NO_2(m)	HNO_3 + H_2SO_4 (4% SO_3)	12·55 13·35	87·45 86·65	87·05	672·2
13	,,	HNO_3 + H_2SO_4 (5% SO_3)	12·25 12·65	87·75 87·35	87·55	703·2
14	,,	Same + $(NH_4)_2SO_4$	14·85 13·95	85·15 86·05	85·60	594·4
15	Ph·CHO	HNO_3 + H_2SO_4 (5% SO_3)	21·60 21·15	78·40 78·85	78·65	368·4

* Compare 80·53% and 413·6% respectively (Baker, Cooper, and Ingold, this vol., p. 426).

† Compare 14·25% and 16·6% respectively (*idem, ibid.*).

‡ See p. 2240.

TABLE II.

	$\frac{m}{o+p}$ (%).		$\frac{m}{o+p}$ (%).
C_6H_5·CH_2Cl	13·35	C_6H_5·CCl_3	160·1
C_6H_5·CH_2·CO_2Et	13·6	C_6H_5·CCl_2·CO_2Et	156·8
C_6H_5·$CHCl_2$	52·25	C_6H_5·CCl$(CO_2Et)_2$	132·6
C_6H_5·CHCl·CO_2Et	43·35	C_6H_5·C$(CO_2Et)_3$	130·1
C_6H_5·CH$(CO_2Et)_2$	34·05	C_6H_5·CH_2Br	7·45
		C_6H_5·CBr$(CO_2Et)_2$	65·05

Discussion of Results.

Application of the Theory of Varying Affinity Demand.—(1) *Relative polar effects of* Cl, CO_2Et, *and* CN. These can be ascertained (compare J., 1909, **95**, 726) from the influence on the dissociation constants of benzoic acid and aniline exercised by these substituents when they occupy the *m*- or *p*-positions. The steric effect from these

positions is negligible, and the alternating effect can be eliminated by averaging the changes in the dissociation constant which a substituent produces when it occupies the *m*-position on the one hand and the *p*-position on the other. It is at present uncertain whether the average change should be calculated by the arithmetical function, polar effect $= (K_m + K_p)/2K_u$, or by the geometrical function, polar effect $= \sqrt{K_m K_p}/K_u$, where K_m, K_p, and K_u are the constants for the *m*- and *p*-derivatives and for the unsubstituted acid (or base) respectively, but the choice of function does not affect the relative order of the polar effects of the above substituents. In connexion with these, the following constants are available :

	K.		*K*.
m-Chlorobenzoic acid	$1{\cdot}59 \times 10^{-4}$	Ethyl *p*-aminobenzoate	$2{\cdot}4 \times 10^{-12}$
p- ,, ,,	$7{\cdot}8 \times 10^{-5}$	Methyl *p*-aminobenzoate	$2{\cdot}9 \times 10^{-12}$
Methyl hydrogen *iso*phthalate	$1{\cdot}28 \times 10^{-4}$	,, *m*-aminobenzoate	$4{\cdot}4 \times 10^{-11}$
m-Cyanobenzoic acid	$1{\cdot}99 \times 10^{-4}$	*m*-Chloroaniline	$3{\cdot}45 \times 10^{-11}$
Benzoic acid	$6{\cdot}0 \times 10^{-5}$	*p*- ,, ...	$9{\cdot}9 \times 10^{-11}$
		Aniline	$4{\cdot}6 \times 10^{-10}$

The constants for ethyl and methyl *p*-aminobenzoate show that ethyl has a slightly greater effect than methyl; and a comparison of methyl *p*- and *m*-aminobenzoates, also of *p*- and *m*-nitrobenzoic acids and of *p*- and *m*-nitroanilines, proves that the effect of *m*-directive substituents is greater in the *p*- than in the *m*-position. Taking this into account, the following polar effects are obtained :

	On benzoic acid.		On aniline.	
	Arithmetical mean.	*Geometrical* mean.	*Arithmetical* mean.	*Geometrical* mean.
m- and *p*-Cl	1·975	1·87	0·145	0·13
m- and *p*-CO_2Me	>2·13	>2·13	0·05	0·025
m- and *p*-CO_2Et	>2·13	>2·13	<0·05	<0·025
m- and *p*-CN	>3·32	>3·32	—	—

The sequence of "negative" polarity is therefore, quite conclusively, $CN > CO_2Et > Cl$, in so far as the effect on the benzene ring is concerned.

(2) *Relative alternating ("quantitative") effects of* Cl, CO_2Et, *and* CN. The affinity demand of methyl-carbon is approximately equal to that of hydrogen, but when it is linked to an atom with higher affinity demand (*e.g.*, in toluene), then an equilibrium is established resulting in an affinity content of the bond between the two which is somewhat greater than in a bond between hydrogen and either of the two atoms; for instance, C_6H_5—C··H·· with ·H·˙ above and ˙·H·. below the C (compare *Chem. and Ind.*, 1925, **44**, 249, and previous papers). Chlorine has a moderate affinity demand, intermediate between those of hydrogen and hydroxyl; when it is attached to an α-methyl carbon atom, it

therefore reduces the affinity content of the bond between the latter and the nuclear carbon atom, but only very *moderately* (see below). Conversely, CO_2Et has an affinity demand only slightly inferior to that of hydrogen (see below); when CO_2Et is attached to α-methyl carbon, the affinity content of the bond between the latter and nuclear carbon is therefore *slightly* raised. Since affinity demand is at its maximum in tervalent nitrogen, the bond between CN and α-methyl carbon has a lower affinity content than the corresponding bonds in either of the other cases, and the affinity content of the bond between methyl and nuclear carbon is correspondingly higher.

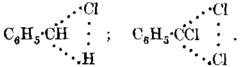
(3) *Resulting directive effects of* Cl, CO_2Et, *and* CN. It follows that the polar factor should cause *m*-substitution in the order $C_6H_5·CH_2·CN > C_6H_5·CH_2·CO_2Et > C_6H_5·CH_2Cl$, and the quantitative factor in the reverse order. In accordance with this, the degree of *m*-substitution has been found to be practically identical in all three cases. On the other hand, when the above substituents are directly attached to the nucleus, *both* factors cause *m*-substitution in the order $C_6H_5·CN > C_6H_5·CO_2Et > C_6H_5Cl$. For the last two compounds this sequence is, of course, a commonplace, but it has now been definitely proved to hold equally for benzonitrile, for which the value obtained by Baker, Cooper, and Ingold (*loc. cit.*) was found to be too low.

(4) *The effects of lateral subsidiary bonds.* A suggestion due to Brühl (*Ber.*, 1907, **40**, 897; compare also Smedley, J., 1909, **95**, 232), according to which there is an exchange of residual affinity (subsidiary bond) between the oxygen atoms of a carboxyl group, appears to have found general acceptance. It explains why the two oxygen atoms in ethyl benzoate—although bivalent and therefore possessed of a marked affinity demand—are barely able to reduce the affinity content of the bond between α- and nuclear carbon to a level below the content of the hydrogen bond in benzene, as shown by the fact that ethyl benzoate still yields about 30% of *o*-, *p*-nitro-derivatives, notwithstanding that its *m*-substitution is also favoured by the polar effect. Brühl's conception, already extended by Smedley (*loc. cit.*) to a subsidiary N–O bond in amides, must logically apply to all cases where two (or more) atoms possess appreciable amounts of residual affinity,* provided, of course, that the partial mutual saturation is not prevented by the spatial factor (distance). The idea explains, for instance, why tellurium hexafluoride is so much less stable than sulphur hexafluoride, since the

* The effect of such residual bonds on aromatic substitution was first recognised in connexion with the lowering of the affinity demand of NH_2 and OH brought about by acetylation (Flürscheim, J., 1909, **95**, 726, footnote).

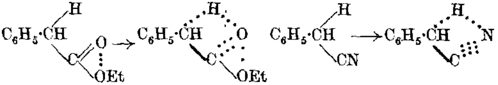
greater distance between the fluorine atoms in the former, due to the greater size of the central atom, involves a lower affinity content in the residual bonds between them. When residual bonds between atoms forming part of α-substituents in toluene are considered in relation to their effects on affinity distribution (and thereby on substitution), it becomes necessary to distinguish between three distinct cases :

(*a*) Cases where residual bonds *lower* the total affinity demand on the α-carbon atom, *e.g.*,



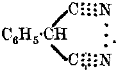
The formulæ show immediately why the alternating effect of the α-chlorine atom is substantially less marked than in the case of nuclear chlorine. Even three α-chlorine atoms can only produce preponderating, but nothing like exclusive, *m*-substitution.

(*b*) Cases where residual bonds *do not affect* the total affinity demand on the α-carbon atom, *e.g.*,



It is seen that in the measure in which the content of the bond between the α-carbon atom and another atom is reduced (broken lines) the affinity content of the bond between the α-carbon and a third atom is increased (thick lines) by the formation of a residual bond.

(*c*) Cases where residual bonds *enhance* the total affinity demand on the α-carbon atom; *e.g.*,



The observation that, whereas nitration of $C_6H_5{\cdot}CH_2{\cdot}CN$ and $C_6H_5{\cdot}CH_2{\cdot}CO_2Et$ yields practically the same $m/(o+p)$-ratio, $C_6H_5{\cdot}CH(CN)_2$ and $C_6H_5{\cdot}CH(CO_2Et)_2$ yield, respectively, ratios of 211·8% and 34·05%, is at first sight puzzling, but is now seen to be a necessary consequence of the theory. The residual bond is here N . . . N and not N . . . H, since the tervalent nitrogen has a much greater residual affinity than the hydrogen atom. Bivalent oxygen has, *ceteris paribus*, always less residual affinity than tervalent nitrogen, and when the carboxyl is compared with the cyano-group this difference is accentuated by the residual neutralisation o

affinity *within* the former group. In $C_6H_5 \cdot CH(CO_2Et)_2$ a residual bond between the two carboxyl groups can therefore not have a marked effect; but in $C_6H_5 \cdot CH(CN)(CO_2Et)$, where a nitrogen atom tends to saturate its residual affinity, the equilibrium principle postulates a more pronounced effect than in the dicarbethoxy-compound, although to a smaller degree than in the dinitrile, and the observed ratio (59·2) is in accordance with this.

It might be thought that the high *m*-ratio from the dinitrile could be due to a primary replacement of the mobile α-hydrogen atom by NO_2, with subsequent migration of the latter into the *m*-position. This possibility has been excluded by nitration of $C_6H_5 \cdot C(CN)_2(CO_2Et)$, resulting in a *m*-ratio of 698·4. This compound and $C_6H_5 \cdot C(CN)(CO_2Et)_2$, both new compounds, constitute two further cases of the examination of directive effects in toluene derivatives in which *all* the α-hydrogen atoms are replaced by substituents which, in direct linking with the nucleus, would be *m*-directive, the first such case investigated having been the nitration of $C_6H_5 \cdot C(CO_2Et)_3$, described in Part VIII.

(5) *Directive effect of* R·N=. It appeared desirable to examine the directive effect of an α-substituent which, in contrast to those already discussed, would combine *weak polarity* with a *high affinity demand*. Such a substituent is to be found in benzylidene-*m*-nitroaniline, which, unlike benzylamine, would even in concentrated acid preserve its nitrogen chiefly in the tervalent state and would not, in contrast to acetylbenzylamine, have the residual affinity of its nitrogen largely neutralised by a subsidiary bond. The group R·N= would obviously exercise a smaller polar effect than O=; if, notwithstanding this, the *m*-ratio were found to be higher for benzylidene-*m*-nitroaniline than for benzaldehyde, the expected effect of the postulated higher affinity demand of tervalent nitrogen would be established. Benzaldehyde, according to Brady and Harris (J., 1923, **123**, 484), in mixed acid yields 81% of *m*-nitro-derivative [$m/(o + p) = 426 \cdot 3\%$], a value with which our own determinations [78·65% *m*-nitration; $m/(o + p) = 368 \cdot 4\%$] are in good agreement, allowing for the difference of method. Schwalbe (*Z. Farb. Textilchem.*, 1902, **1**, 628) obtained essentially *m*-nitro-benzaldehyde from benzylidene-*m*-nitroaniline in mixed acid, but he neither determined the proportions of the isomerides formed, nor showed whether or not hydrolysis to the aldehyde *preceded* nitration.

Our own experiments prove that in the absence of hydrolysis, in a still stronger acid than Schwalbe's, the *m*-percentage 87·5 [$m/(o + p) = 703\%$] is obtained (nitration No. 13); that the compound during nitration is largely present as the *free* anhydro-base,

as shown by the intensely yellow colour of its solution in concentrated sulphuric acid, compared with its colourless *hydrochloride* obtained by precipitating the base with dry hydrogen chloride; and that the high *m*-ratio is not attributable to nitration of the *m*-directive cation (compare Part V) of the sulphate of the anhydro-base. This last fact was established by testing the effect of added ammonium sulphate on the *m*-ratio, since *m*-nitration of the cation would thereby be appreciably reduced by what Pollard and Robinson (J., 1927, 2770) have named the "Flürscheim effect." A comparison of nitrations Nos. 13 and 14 with Nos. 7 and 8 of Part V (J., 1926, 1569) shows that in the present case, notwithstanding a slightly higher concentration of ammonium sulphate, this effect is very much less marked than with diethylbenzylamine. This is what would be expected since, on the basis of *any* theory, even that relatively small portion of the very weak base benzylidene-*m*-nitroaniline which may be present as salt will be less *m*-directive (according to us, less electrolytically dissociated) than the diethylbenzylammonium salt, and since even the latter, at similar concentration, is chiefly *o*-, *p*-directive. Obviously, the presence of any benzylidene-*m*-nitroaniline as sulphate would therefore *lower* the *m*-ratio, and the value for the latter found in nitration No. 14 must be regarded as a lower limit for the free anhydro-base. *The greater affinity demand of nitrogen in this compound thus clearly outweighs the higher polarity of oxygen in benzaldehyde.*

Conclusion.

The theory of varying affinity demand, relying on one single mechanism, provides a consistent interpretation of our observations. When we examine the results recorded in this paper in the light of the electronic theory of valency, we find that our remarks in Part VIII (this vol., p. 1609, last sentence of section 3) appear to apply with even greater force. It is, however, by considering the effect of substituents on *equilibria* (electrolytic and thermal dissociation) that we hope to obtain a clear-cut decision between these ideas, since the effect of a passing phase (conjugation) on a permanent equilibrium must be negligible, so that one of the two alternative electronic mechanisms can be eliminated.

EXPERIMENTAL.

Preparation of Materials.—(*a*) *Ethyl phenylcyanomalonate.* 15 G. of ethyl phenylacetate and 1·5 g. of sodium wire in 50 c.c. of dry ether were left over-night, and 10 c.c. of ethyl chloroformate were then added. On shaking, the white crystalline sodium salt gradually changed to a jelly-like mass. After the suspension had been shaken

for 7 hours and kept over-night, water was added, and the ethereal layer dried and distilled; 15 g. of a thick oil were obtained which, on redistillation, boiled at 140—141°/1 mm. (Found: C, 64·4; H, 5·8; N, 5·3. $C_{14}H_{15}O_4N$ requires C, 64·4; H, 5·8; N, 5·4%).

(*b*) *Ethyl phenyldicyanoacetate.* 4 G. of phenylmalonitrile and 0·8 g. of sodium in 75 c.c. of dry absolute ether were left for 20 hours. Evolution of hydrogen was slow. After filtration, the white sodium salt was separated mechanically from unchanged sodium, introduced into 40 c.c. of sodium-dried benzene, and 5 c.c. of ethyl chloroformate were added. After 7 hours' shaking and standing over-night, a gelatinous mass had formed. The whole was then shaken with water, the benzene layer separated, and the benzene removed at reduced pressure. On recrystallising the residue from alcohol, 4·9 g., m. p. 58—59°, were obtained, showing after further recrystallisation the constant m. p. 60° (mixed m. p. depression with phenylmalononitrile) (Found: C, 67·2; H, 4·9; N, 13·3. $C_{12}H_{10}O_2N_2$ requires C, 67·3; H, 4·7; N, 13·1%).

(*c*) Phenylmalononitrile was prepared according to Hessler (*Amer. Chem. J.*, 1904, **32**, 119), who obtained it from dilute alcohol with m. p. 68—69°. By using absolute alcohol, we found m. p. 70—71°. Benzylidene-*m*-nitroaniline had m. p. 72·5—73°; benzyl cyanide, b. p. 229—230°; benzonitrile, b. p. 190—191°; mandelonitrile solidified at 5°, m. p. 13° (clear); ethyl phenylcyanoacetate, b. p. 125—126°/1 mm.; α-chlorobenzyl cyanide, b. p. 135—136°/40 mm.

Methods.—(*a*) *Nitration.* The experimental conditions and yields for each nitration are given in Table III. Apart from the nitrations of benzylidene-*m*-nitroaniline (see below), where hydrolysis on subsequent dilution withdrew most of the aniline portion of the anhydro-base from the weighings, the yields were excellent in all cases.

(*b*) *Determination of the isomerides.* Oxidation of the products of nitration to the acids was carried out as described in Part VIII. Ethyl phenylcyanomalonate, however, like ethyl phenylmethanetricarboxylate, had to be treated differently (see below). Our remark (this vol., p. 449) that our modification of the permanganate method had not failed in a single instance must therefore, in the light of our subsequent experience, be qualified in the sense that compounds which—owing to steric inhibition—are exceptionally resistant to lateral oxidation are prone to nuclear destruction by permanganate. It appears that, in such cases, Baker and Ingold's modification of the nitric acid method, *followed* by the application of our modification of the permanganate method, gives trustworthy results. The composition of the acids obtained was in all cases determined by our method described in Part VI.

No.	G.	Medium.	Temp.	Time.	Yield, g.	$KHCO_3$-soluble, g.	Oxidised, g.	Yield of acids, g.	Reduction and bromination … Used, g.	Found (g.) Benzoic acid.	Found (g.) Tri-bromo-aniline.	Found (g.) Tribromo-amino-benzoic acid.	Appearance of nitration product.
1	9·370	75 g. HNO_3	−10 to −8°	1 hr. for adding; 30′ at −10°, 15′ room.	8·440 +4·70	+0·146	1·732 1·732	1·722 1·754	1·722 1·754	0·011 0·008	1·127 1·117	2·521 2·673	The 8·440 g.=pure m-nitro-deriv., m. p. 117·5°.
2	11·20	90 g. HNO_3	−10 to −8°	1½ hrs. for adding; 15′ at −10°, 15′ room.	14·658	+0·129	3·664 3·664	1·953 p- (m. p. 233—235°) +1·030 1·958 p- (m. p. 234—236°) +1·388	1·030 0·500	0·004 0·003	1·254 0·707	0·878 0·334	Yellow solid.
3	7·020	56 g. HNO_3	−10 to −8°	10′ for adding; 40′ at −10°, 15′ room.	8·50	—	3·525 2·660	1·742 1·385	1·000 1·000	0·004 0·007	1·216 1·212	0·825 0·805	Pale yellow oil.
4	3·400	27·2 g. HNO_3	−10°	30′ for adding; 45′ at −10°, 15′ room.	4·495	—	2·000	1·525	1·000	0·006	0·600	1·512	Brownish-yellow solid.
5	2·900	46 g. HNO_3	−5 to 0°	15′ for adding; no standing.	1·452 + 2·331	—	1·000 1·500	0·520 0·794	0·500 0·500	0·018 0·002	0·359 0·294	0·675 0·778	Brownish oil. Oil, solid on standing.
6	3·000	24 g. HNO_3	18—20°	15′ for adding; 5′ at 20°.	1·123 + 2·565	—	1·123 1·560	0·510 0·769	0·500 0·500	0·009 0·003	0·341 0·301	0·670 0·766	Brownish oil. Oil, solid on standing.
7	7·930	63·5 g. HNO_3	−10 to −8°	30′ for adding; 45′ at −10°, 15′ room.	9·200	+0·127	3·775 2·543	1·348 0·776	1·000 0·500	0·009 0·005	0·582 0·301	1·552 0·759	Thick, pale yellow oil.
8	4·500	36 g. HNO_3	−10°	10′ for adding; 25′ at −10°, 60′ room.	5·280	+0·094	1·912 1·990	0·721 0·711	0·500 0·500	0·026 0·019	0·109 0·118	0·899 0·889	Pale yellow solid (on standing).
9	7·750	62 g. HNO_3	−10 to −8°	60′ for adding; 30′ at −10°, 15′ room.	9·590	+0·141	3·111	2·117	1·000	0·004	0·904	1·193	Slightly yellow solid.
10	3·510	28 g. HNO_3	−10 to −8°	20′ for adding; 5′ at −10°.	4·390	+0·051	2·857	1·765	1·765	0·042	1·565	1·778	
11	8·140	65 g. HNO_3	−10 to −8°	60′ for adding; 30′ at −10°, 15′ room.	8·070	+2·288	2·940 2·720	2·172 1·976	1·000 1·000	0·005 0·004	1·097 1·110	0·971 0·960	Pale yellow. Nearly solid.
12	13·200	72 g. H_2SO_4 (4% SO_3) +4·1 g. HNO_3	10°	24 hrs. at room temp.	10·056	—	2·020 2·017	1·621 1·629	1·000 1·000	0·005 0·004	0·245 0·260	1·932 1·910	Dark brown solid.
13	8·000	44 g. H_2SO_4 (5% SO_3) +1·2 g. HNO_3	10°	24 hrs. at room temp.	3·677	—	2·025 1·601	1·606 1·220	1·000 1·000	0·510 0·501	0·117 0·121	0·952 0·947	Dark brown oil.
14	7·400	41 g. H_2SO_4 (5% SO_3) +1·1 g. HNO_3 +11 g. $(NH_4)_2SO_4$ …	10°	24 hrs. at room temp.	3·772	—	1·972 1·700	1·587 1·405	1·000 1·000	0·485 0·470	0·146 0·138	0·950 0·966	
			10°	24 hrs. at room …	7·449	+0·228	2·700 2·260	2·639 2·220	1·000 1·000	0·484 0·478	0·219	0·898	Pale yellow oil.

Details of Nitrations.—The conditions and actual weighings in connexion with the nitrations are to be found in Table III, in which the numbers in column 1 correspond with those in column 1 of Table I. The following additional information appears desirable.

Benzonitrile (No. 1). By pouring the nitration product on ice, 1·521 g. of precipitate, m. p. 108—111°, were obtained, and by xtracting the filtrate with ether a further 1·621 g. were recovered hich solidified on standing. By recrystallising the 11·521 g. twice rom water, 8·440 g. of pure *m*-nitrobenzonitrile (m. p. 117·5°) were btained. The mother-liquors together with the above 1·621 g. ere in this case not oxidised, but hydrolysed to the acids by boiling part for 8 hours with 9 parts of 15% hydrochloric acid, and comleting the hydrolysis by boiling with 0·15 part of permanganate nd a little potassium hydroxide in 15 parts of water for 1½ hours.

Ethyl phenylcyanoacetate (No. 3). Nitration in acetic anhydride duced the *m*-percentage in this case as in phenylmalononitrile, but ot nearly to the same extent, no doubt on account of the less proounced reactivity of the side-chain. Two nitrations in acetic nhydride (one shown in parentheses) gave, from 1·000 (0·700) g. of xidation acids, 1·000 (0·865) g. of tribromoaniline and 0·640 (0·514) . of tribromoaminobenzoic acid.

Phenylmalonitrile (Nos. 4—6). That nuclear nitration was ractically complete, followed from the results of the reduction nd bromination of the acids. To eliminate the possibility that he high *m*-percentage might in part have been due to another itro-group having become attached to the α-carbon atom prior to uclear nitration, experiment No. 4 was repeated and the freshly repared nitration *product* brought to constant weight in a vacuum ver caustic potash (Found: C, 56·5; H, 2·6. $C_9H_5O_2N_3$ requires , 57·7; H, 2·7%). The product therefore contained only *one* itro-group. In nitrations Nos. 5 and 6, the product of nitration as extracted with benzene before being extracted with ether as sual. The upper figures in the column headed "Yield" in Table I are the weights of the benzene extracts, the lower figures being ose of the ether extracts for these two nitrations. Nitration of enylmalononitrile in the presence of acetic anhydride appeared to preceded by some side-chain reaction, since the preponderating -nitration observed in its absence was completely reversed. Thus 9 g. of phenylmalononitrile in 7·9 c.c. of acetic anhydride, to which a ixture of 8 g. of acetic anhydride and 8 g. of nitric acid (*d* 1·52) was ded at 15—20° during 20 minutes, with subsequent standing for minutes, yielded 10·35 g. of a whitish, solid mass. This gave the llowing results on oxidation (those of a second oxidation are added parentheses): 2·14 (2·45) g. of nitration product gave 1·123

(1·325) g. of acids; 1·000 (1·000) g. of these gave 0·203 (0·193) g. of benzoic acid, 1·392 (1·412) g. of tribromoaniline, and 0·102 (0·110) g. of tribromo-*m*-aminobenzoic acid, thus indicating almost exclusive *o*-, *p*-substitution.

Ethyl phenylcyanomalonate (No. 7). On adding this substance to the nitrating acid, a pale red colour was produced, which gradually changed to green. Oxidation by permanganate yielded only 0·2 g. of acids from 2·3 g. of nitration product, but when 3·775 g. of the latter were boiled for 4 hours with 40 c.c. of nitric acid (*d* 1·125) and then successively with 2 g. and 1 g. of permanganate, a yield of 1·348 g. of acids (nearly 70% of the theoretical) was obtained.

Ethyl phenyldicyanoacetate (No. 8). A cyano-group being smaller than a carbethoxyl group, oxidation by permanganate succeeded in this case, but the yields were still not quite as good as usual. The nitration product, *ethyl* m-*nitrophenyldicyanoacetate*, a pale yellow solid, gave a deep red colour in alcohol, and in dilute acetone. It crystallised from alcohol in white crystals, m. p. 130—133·5°, from chloroform with m. p. 133—134·5°, and from benzene with m. p. 132—134°. In all three cases the fused specimens were *red*, and lost this colour on solidification; they were soluble in cold alcohol or acetone with a strong reddish-orange colour, which deepened on adding water, but the solution in benzene or chloroform was colourless (Found: N, 16·68. $C_{12}H_9O_4N_3$ requires N, 16·22%).

a-Chlorobenzyl cyanide (Nos. 9 and 10). Nitration in acetic anhydride at 15° only took place to the extent of about 1·5%. Since, moreover, other α-cyano-compounds behaved abnormally in this medium, it became necessary to operate in nitric acid (*d* 1·52) alone, although appreciable hydrolysis could not be avoided. In No. 9 the spent acid gave 1·2401 g. AgCl, corresponding to 16·9% of hydrolysis, and in No. 10, where exposure to the acid was shorter, 0·3306 g. AgCl (hydrolysis = 10·0%). The calculated *m*-figures (marked ‡) in Table I have therefore been based on No. 10 alone. Since No. 9, with greater hydrolysis, gave a higher *m*-percentage than No. 10, whereas mandelonitrile yielded a lower *m*-percentage than No. 10, it is obvious that a product other than mandelonitrile is initially formed by hydrolysis, and nitrated. This can only be mandelonitrile nitrate. This result is entirely in agreement with the high *m*-percentage observed in the nitration of benzyl bromide in nitric acid alone (see Part VIII); in this case benzyl nitrate must have been the initial product of hydrolysis, since benzyl alcohol would obviously lead to even less *m*-derivative than mandelonitrile. On adding α-chlorobenzyl cyanide to nitric acid, a red colour was observed, which disappeared on shaking.

Benzylidene-m-nitroaniline (Nos. 12, 13, and 14). The yields

given in Table III were obtained by pouring the acid, without cooling, into water in order to hydrolyse most of the anhydro-base and leave the aniline portion in solution. The aldehyde portion was extracted with benzene. The fact that no appreciable hydrolysis occurred during nitration, even in No. 12 where only 4% SO_3 was present as against 5% in Nos. 13 and 14, was proved by pouring exactly one-half of the acid from No. 12 on a mixture of ice and excess of bicarbonate, whereupon 7·044 g., m. p. 142—143°, were precipitated. From 1 g. of this ochre-coloured product, recrystallised from petrol (b. p. 100—120°), 0·710 g. of almost pure *m*-nitrobenzylidene-*m*-nitroaniline, m. p. 148—154°, mixed m. p. higher, was obtained. A synthetic sample prepared by us had m. p. 160° (literature 153°). The yield given in No. 12 is double the amount recovered from the remaining half of the acid by pouring it into water. The proportion of nitric acid used in Nos. 13 and 14 was only one-half of that in No. 12. That no appreciable portion of the anhydro-base would be sulphonated in our conditions appeared probable from the stringent conditions which Schwalbe (*loc. cit.*) had to resort to for its sulphonation. We have confirmed this by leaving the base (5·5 g.) in 5% oleum (30 g.) for 2 hours at room temperature, then pouring it into 50 c.c. of water, whereby 2·313 g. of benzaldehyde were recovered.

In order to prove that the tendency to salt formation in benzylidene-*m*-nitroaniline is even less than in *m*-nitroaniline (which in turn is already millions of times weaker than diethylbenzylamine, the salt solution of which is still chiefly *o*-, *p*-directive under similar conditions), a comparison was made of the relative thermal stabilities of the *hydrochloride* of benzylidene-*m*-nitroaniline with that of *m*-nitroaniline. The former salt was obtained by passing dry hydrogen chloride through a solution of 1 g. of the base in 30 c.c. of dry benzene, and keeping the filtered salt for 48 hours in a desiccator over potassium hydroxide [Found: Cl (Carius), 13·5. $C_{13}H_{11}O_2N_2Cl$ requires Cl, 13·5%]; this salt is colourless. Carbon dioxide (purified by passage successively through water, silver nitrate solution, and concentrated sulphuric acid) was passed through flasks containing the two hydrochlorides, which were immersed side by side in an oil-bath. Until the temperature of the bath reached 110° no silver chloride was deposited in 2 hours in silver nitrate solutions through which the carbon dioxide passed on leaving the flasks. At 120° the benzylidene-*m*-nitroaniline salt began to give off hydrogen chloride, whereas the *m*-nitroaniline hydrochloride was still stable at 145°, and only began to yield a deposit at 150°. The anhydro-base could be recovered mostly unchanged by shaking 0·200 g. of the salt with benzene and potassium bicarbonate solution until

everything was dissolved. The dried benzene solution left 0·174 g. of the base (m. p. 55—57·5°, mixed m. p. 57—59·5°).

We desire to express our indebtedness to the Advisory Council of the Department of Scientific Research, and to the Government Grant Committee of the Royal Society, for grants to one of us (E. L. H.); also to Sir W. H. Bragg and the Royal Institution, who have placed at our disposal the facilities of the Davy Faraday Laboratory, where the work was carried out.

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CCXCI.—*The Solubility of Potassium Ferricyanide in Water between* 0° *and* 100°.

By John Albert Newton Friend and William Nelson Smirles.

Vallance (J., 1927, 1328) found a break in the solubility curve of potassium ferrocyanide in water at approximately 18°. This did not appear to be connected with any change in hydration of the solid phase, and is of particular interest in view of the long-admitted possibility of the existence of two stereoisomeric forms of the salt (Briggs, J., 1911, **99**, 1019; 1920, **117**, 1026; Bennett, 1917, **111**, 490).

When the solubility curve of potassium ferricyanide is drawn from the six results of Wallace (J., 1855, **7**, 80) and the one datum of Schiff (*Annalen*, 1860, **113**, 150) for 13°, a break would appear to occur between 20° and 40°. The solution-density curve likewise suggests a break. In view of the alleged isomerism of the salt (Locke and Edwards, *Amer. Chem. J.*, 1899, **21**, 193, 413; but see Bellucci and Sabatini, *Atti R. Accad. Lincei*, 1911, **20**, 1; Piutti, *Ber.*, 1912, **45**, 1830; Hauser and Biesalski, *Ber.*, 1912, **45**, 2516; Wells, *Amer. Chem. J.*, 1913, **49**, 205; Briggs, J., 1920, **117**, 1026), a further investigation of this point appeared to be desirable.

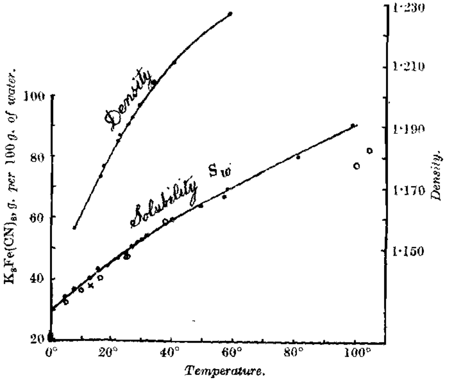
Experimental.

Pure potassium ferricyanide was recrystallised, and its iron content was estimated by decomposing about 0·5 g. with concentrated sulphuric acid in a platinum dish, heating until the colour that developed had disappeared, adding a small quantity of concentrated nitric acid, and again heating until sulphuric acid fumes were freely evolved. After cooling, the residue was dissolved in dilute hydrochloric acid, diluted to approximately 400 c.c., and the ferric hydroxide precipitated with ammonia, filtered, re-dissolved, repre-

cipitated, ignited, and weighed [Found: Fe, (i) 17·08, (ii) 17·01. Calc.: Fe, 16·96%].

Determination of Solubility.—The method employed in preparing a saturated solution was similar to that described by Lumsden (J., 1902, **81**, 350). The solution was stirred continuously in contact with the finely crushed salt for about 6 hours, a portion being withdrawn by suction from the saturation bottle through glass wool into a receiving flask, the usual precautions for submersion

Fig. 1.



Solubility and density curves of $K_3Fe(CN)_6$.

○ Wallace's data.
× Schiff's datum [38 g. $K_3Fe(CN)_6$ per 100 g. H_2O].
⦶ Grube's result (*Z. Elektrochem.*, 1914, **20**, 342).

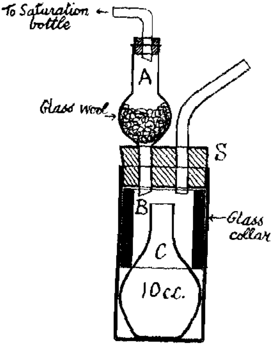
in the thermostat being observed to ensure complete uniformity of temperature. A measured volume of the filtered solution was diluted to 250 c.c., and 25 c.c. were evaporated to dryness; from the iron content, determined as indicated above, the amount of ferricyanide was calculated.

The results are given in Fig. 1 and Table I, where S_w and S_s represent g. of anhydrous salt per 100 g. of water and of solution respectively.

Determination of Density.—For the determination of the density of the saturated solution, the apparatus shown in Fig. 2 was attached to the saturation bottle, and the liquid sucked over. The apparatus

consisted of a 10 c.c. glass density bottle, C, standing inside a closely fitting cylindrical bottle, and kept in position either with a glass rod through the rubber stopper S, or by a loose glass collar as shown in the figure. The volume of C and its variation with temperature had previously been ascertained. The end B of the filter tube A was adjusted not to pour direct into C but *outside it*, and then to flow into it as the containing bottle filled up. The rubber stopper was now removed, and the glass stopper inserted in the density bottle, which was then washed and set aside to cool, being covered with a small tube to prevent evaporation through the capillary.

Fig. 2.



After a density determination the solution was frequently used for a solubility determination so that both data were obtained from the one sample. The results (in air) are given in Table I.

Table I.

Temp.	S_w.	S_t.	$D_4^{t°}$ (in air).	Temp.	S_w.	S_t.	$D_4^{t°}$ (in air).
0·1°	30·24	23·22	—	28·3°	52·14	34·27	—
4·7	34·21	25·49	—	28·9	—	—	1·1071
7·8	36·95	26·96	1·1567	29·8	53·02	36·65	—
12·8	40·22	28·68	—	31·5	54·21	35·15	—
15·7	43·58	30·35	1·1738	33·1	—	—	1·2045
16·75	—	—	1·1766	39·9	59·27	37·22	1·2115
18·7	44·85	30·96	—	49·0	64·25	39·12	—
21·8	—	—	1·1855	56·25	67·80	40·41	—
22·1	47·22	32·08	1·1872	58·0	69·78	41·10	1·2269
25·0	48·80	32·80	—	81·0	80·82	44·70	—
25·3	—	—	1·1905	99·0	90·83	47·60	—
26·3	50·74	33·66	1·1928				

Discussion.—The density and solubility data (S_w) are shown in Fig. 1. The curves are regular, giving no indication of a break. The solubility curve conforms to the equation

$$S_w = 30{\cdot}4 + 0{\cdot}80t - 0{\cdot}0020t^2.$$

With the exception of the value at 37·8°, Wallace's figures are lower than ours, particularly that at 100°, probably owing to the fact that he

estimated his ferricyanide volumetrically by reduction with stannous chloride, a method that is less accurate than the gravimetric. The very low results at 100° and above may possibly be in part due to hydrolysis. Even warm solutions smell of hydrocyanic acid, and at 100° the odour is very marked. Hydrolysis would be likely to affect the volumetric method more seriously than the gravimetric. In order to reduce the disturbing effect of any such change we were careful to use fresh solutions for each of our determinations. Schiff's result is a little low. Grube states that one litre saturated at 25° contains 385·5 g. of salt, and if our mean value (1·1905) be adopted for the density at this temperature, S_w is 47·89, a value slightly lower than ours, *viz.*, 48·80.

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CCXCII.—*Lithium Sulphite and some Derivatives.*

By JOHN ALBERT NEWTON FRIEND and DONALD WHITWORTH POUNDER.

PUBLISHED data concerning lithium sulphite are both scanty and unsatisfactory. Danson (J., 1848, **2**, 207) appears to have been the first to prepare the hydrated salt. He passed sulphur dioxide into an aqueous suspension of lithium carbonate until a colourless solution was obtained, and precipitated the hydrated sulphite either by addition of alcohol or by boiling to expel excess of sulphur dioxide. He noticed its ready oxidisability.

Apparently the only other investigator was Röhrig (*J. pr. Chem.*, 1888, **37**, 225), who believed he had isolated both a mono- and di-hydrate, the former by methods similar to those of Danson, the latter by precipitation with alcohol from strongly acid solution. Röhrig's research is the one usually quoted, and there can be no doubt that he obtained a hydrate of lithium sulphite, but the inadequate nature of his analyses appears to have escaped observation. The lithia was correctly estimated as sulphate, but the sulphur dioxide content was calculated after oxidation to sulphate and weighing as barium or lead sulphate. The amount of oxidising agent required was not ascertained, and no tests are recorded to prove the absence of sulphate. In view of the ready oxidation of the salt, this was a singular omission, for it is evident that the ratio $Li_2O : SO_2$, as calculated by the above method, would be the same for the known *sulphates*, Li_2SO_4 and Li_2SO_4,H_2O, as for the supposed *sulphites*. Further, since the water was calculated by difference, the analyses were insufficiently complete to distinguish between

Li_2SO_4 and Li_2SO_3,H_2O, on the one hand, and between Li_2SO_4,H_2O *and* $Li_2SO_3,2H_2O$, *on the other. Moreover, since the higher hydrate* was alleged to be formed from the more strongly acid solution, we deemed it desirable to re-investigate the subject.

We have confirmed the existence of the monohydrate, but have obtained no clear evidence of a dihydrate: it is possible that Röhrig's salt was the monohydrate imperfectly freed from water and/or alcohol, for it retains these substances very tenaciously. We have also prepared the *pure anhydrous* salt for the first time, and although we have not been able to isolate the hydrogen sulphite, we have prepared its *compounds* with aldehydes and ketones.

EXPERIMENTAL.

The *monohydrate*, Li_2SO_3,H_2O, is readily prepared by making lithium carbonate into a very thin cream with water and passing a mixture of sulphur dioxide and purified hydrogen through it at room temperature with shaking, access of air being prevented with water seals. The object of the hydrogen is to avoid inrush of air during absorption of sulphur dioxide and passage of the liquid up the delivery tube when the supply of the latter gas is cut off. Passage of the sulphur dioxide is continued until the whole of the lithium carbonate has passed into solution and effervescence has ceased, but too great excess should be avoided. The sulphite may be separated in one of the following ways:

1. Evaporation on the water-bath, care being taken to minimise oxidation (see analysis *a*). Unless pure sulphite is required this is *a rapid and convenient method of preparation.*

2. Evaporation over concentrated sulphuric acid in a vacuum: this is tedious, but yields a very pure, crystalline product (see analyses *b* and *c*).

3. Pouring the solution into excess of alcohol, whereby a white precipitate is obtained which is somewhat difficult to filter, particularly when excess of sulphur dioxide is present. The precipitate is washed with alcohol and ether, and may be dried at 100° or preferably at room temperature in a vacuum desiccator over sulphuric acid: with care, the latter procedure gives a white powder entirely free from sulphate (analysis *d*).

As obtained by the above methods, the monohydrate is readily soluble in water. When exposed to water vapour in the absence of air the salt steadily increases in weight and finally deliquesces to a colourless solution. Exposed to air, it slowly oxidises to sulphate even in a desiccator. Thus, a specimen of the pure salt after keeping for 8 days contained only 46·20% SO_2, and this fell, after a further 7 days, to 36·76% (Calc. for Li_2SO_3,H_2O, 57·22%).

In dilute solution, the salt oxidises rapidly; an $M/10$-solution exposed to air oxidised somewhat less rapidly than equivalent solutions of the sodium and potassium salts.

The monohydrate retains its water over sulphuric acid at room temperature, but becomes anhydrous at 180°, undergoing slight oxidation to sulphate if exposed to air during heating. Numerous analyses of the different batches of salts have been made, the lithium being estimated as sulphate, and the sulphur dioxide iodometrically. The water is usually calculated by difference. Typical analyses are as follows:

	a.	*b.*	*c.*	*d.*	Theory.
Li_2O (%)	27·42	25·37	26·28	27·29	26·69
SO_2 (%)	56·85	54·39	56·35	57·66	57·22
H_2O (by diff.) (%)	15·73	20·24	17·37	14·90	16·09
Ratio Li_2O/SO_2	0·4823	0·4664	0·4664	0·4733	0·4664

Salt *b* was quite free from sulphate, but retained some adsorbed moisture. Salt *c* contained a trace of sulphate but less adsorbed water, having been kept in a vacuum desiccator for a longer period than the preceding salt. Salt *d* was prepared by the third method, sulphur dioxide being present in only very slight excess. While in the vacuum desiccator, it was repeatedly "rinsed" with air until it ceased to smell of ether. It was entirely free from sulphate but contained 0·15% of iron, calculated as Fe_2O_3.

Following Röhrig's procedure for the preparation of the supposed dihydrate, sulphur dioxide and hydrogen were passed into an aqueous suspension of lithium carbonate until a yellow, acid solution was obtained, the yellow colour indicating the presence of acid sulphite in solution. This was poured into excess of alcohol, and the precipitated salt filtered off (with difficulty) at the pump. A portion was analysed immediately and contained 72·02% of alcohol plus water. Had it not contained alcohol, this would have corresponded to $Li_2SO_3,14H_2O$, which requires H_2O, 72·86%. It was not a definite compound and lost weight rapidly in the balance case. The remainder, when placed on a clock glass in a vacuum desiccator over sulphuric acid, continuously lost weight for 24 hours, but then remained practically constant and was analysed. All the alcohol had evaporated, and the salt consisted of lithium sulphate monohydrate with a trace of sulphate (Found: H_2O, 15·71. Calc.: 16·09%).

Anhydrous lithium sulphite, Li_2SO_3, is conveniently prepared in a pure state by passing a mixture of sulphur dioxide and purified hydrogen into a cream of lithium carbonate and water until effervescence ceases. The flask is then heated to 180—200° in an oil-bath, dry hydrogen being passed through until the salt is anhydrous.

Thus obtained, lithium sulphite is a dull white powder, more stable than the *monohydrate*. A sample kept in a desiccator for a month was free from all but a trace of sulphate (Found: Li_2O, 31·84; SO_2, 67·72; H_2O, 0·38; total, 99·94; $Li_2O:SO_2$, 0·4702. Li_2SO_3 requires Li_2O, 31·81; SO_2, 68·19%; $Li_2O:SO_2$, 0·4664).

The salt melts at approximately 455° and undergoes partial decomposition, yielding a brown, green, or blue mass according to circumstances. If air is excluded, some lithium sulphide appears to be formed, for the product smells of hydrogen sulphide. This was observed by Röhrig, who suggested the reaction: $4Li_2SO_3 = 3Li_2SO_4 + Li_2S$. An analogous reaction has since been shown to take place on heating sodium sulphite at 700° in a vacuum (Picon, *Compt. rend.*, 1924, **178**, 1548).

Organic Derivatives of Lithium Hydrogen Sulphite.

Acetone. A thin cream of lithium carbonate and water was covered with acetone in a flask, and sulphur dioxide diluted with hydrogen passed through. The temperature rose slightly and after all the carbonate had decomposed a white, crystalline derivative formed. This was washed with acetone and ether. The lithium content was determined by heating with concentrated sulphuric acid and weighing as sulphate (Found: Li_2O, 9·03. $LiHSO_3,C_3H_6O$ requires Li_2O, 9·11%). The acetone was estimated iodometrically; the method did not appear to be very accurate, but sufficed to show that at least 93% of the theoretical quantity of acetone was present. After two months in a stoppered bottle, analysis gave Li_2O, 9·12%; but in another sample that had been less securely stoppered, the percentage of Li_2O rose in a few weeks to 13·57, and the residue smelt of sulphur dioxide, indicating appreciable decomposition.

Benzaldehyde. This derivative was obtained in a similar manner as a beautifully white product; it smelled strongly of benzaldehyde, which was rapidly evolved on warming (Found, for two specimens: Li_2O, 7·14, 8·61. Li_2HSO_3,C_7H_6O requires Li_2O, 7·70%).

Acetaldehyde gave a white product, not analysed. Acetophenone did not react.

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CCXCIII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXVIII. The Preparation and some Properties of Benzyl Fluoride.*

By Christopher Kelk Ingold and Edith Hilda Ingold.

Although benzyl chloride, bromide, and iodide are familiar substances, the preparation of benzyl fluoride has not yet been described, and, in view of the importance of the benzyl halides for the study of serial relationships in the electrochemical behaviour of the halogen elements in organic chemistry, we attempted to devise a satisfactory method for the formation of the missing member of the series. Recent imperfectly successful attempts have been recorded by Tronov (*J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1270), who treated benzyl chloride with silver fluoride and obtained only toluene, and by Swarts (*Bull. Soc. chim.*, 1924, **35**, 1533), who, by some method not stated, obtained "with great difficulty" a small quantity of a liquid which was neither purified nor analysed, and quickly decomposed.

In their study of the decomposition of quaternary ammonium salts, Hanhart and Ingold (J., 1927, 997) showed that under structural conditions antagonistic to the formation of an olefin, the alkyl radical most tolerant to a positive charge is ejected and subsequently combines with the anion of the salt. The order of toleration given included the inequality $C_6H_5{\cdot}CH_2 > CH_3$, and the present application is that the distillation of a quaternary ammonium fluoride such as benzyltrimethylammonium fluoride, containing only benzyl and methyl groups, should yield a predominating proportion of benzyl fluoride. We have prepared benzyl fluoride from several salts of this type (yields about 60% after complete rectification) and have taken the opportunity to study its properties.

Benzyl fluoride is a colourless liquid with an odour which is quite unlike that of its analogues, and rather resembles that of benzene. The m. p. is $-35°$, and the b. p. 139·9°/760 mm. is of interest in relation to those of toluene, benzal fluoride, and benzotrifluoride. The series $C_6H_5{\cdot}CH_3$(110·8°), $C_6H_5{\cdot}CH_2F$(139·9°), $C_6H_5{\cdot}CHF_2$(133·5°), $C_6H_5{\cdot}CF_3$(103·5°) shows a maximum at the boiling point of benzyl fluoride, and this is noteworthy in relation to Arkel and de Boer's theory respecting the boiling points of organic compounds (*Physica, Nederlandsch Tijdsch. Natuurkunde*, 1924, **4**, 392; 1925, **5**, 134; *Rec. trav. chim.*, 1925, **44**, 675). According to these authors, the boiling points of halogenohydrocarbons are additive in the sense that they can be expressed as a simple function of the sum of a number of terms ("$\sqrt{\alpha}$-values") corre-

sponding to the contributions of the atoms to the external molecular field and hence to the internal pressure of the liquid. For compounds belonging to the same hydrocarbon type the $\sqrt{\alpha}$-values of the halogens are constant; *e.g.*, for methane derivatives the values are F 23, Cl 47·5, Br 60·8, I 81·3. On the other hand, the $\sqrt{\alpha}$-value for hydrogen is variable and depends upon the degree of incipient ionisation induced by the halogen atoms attached to the same carbon atom. The degree of incipient ionisation produced by different halogens is substantially the same, and therefore the main factor which determines the $\sqrt{\alpha}$-value for hydrogen is the number of halogen atoms attached to the carbon atom to which it is linked. The following $\sqrt{\alpha}$-values for hydrogen illustrate this (X = halogen): CH_4 16·2, CH_3X 21·4, CH_2X_2 25·2, CHX_3 26·1. The peculiarity of fluorine is that its $\sqrt{\alpha}$-value lies within the range of values which hydrogen may assume, and hence the possibility arises that whilst the replacement of one hydrogen atom in a hydrocarbon by fluorine may cause an increase in $\Sigma\sqrt{\alpha}$ and thus an increase in boiling point, the replacement of succeeding hydrogen atoms attached to the same carbon atom may lead to a decrease both in $\Sigma\sqrt{\alpha}$ and in the b. p. The series of b. p.'s given above forms a striking illustration of this deduction, and is the first complete series of the kind. As already stated, the $\sqrt{\alpha}$-values vary slightly from type to type, and it must be assumed that the value for side chain hydrogen crosses the fluorine figure on passing from toluen to benzyl fluoride, thus producing a maximum b. p. at this membe of the series.

We have studied the refraction and the dispersion of benz fluoride, both because these data will ultimately be required f the calculation of the molecular dipole moment of this substanc and also because the effect of the substituent (F) on the optic dispersion of a substance forms a partial measure of its effect the rigidity of the electrons in the molecule. To facilitate accurate comparison of the refraction constants of fluorine relati to those of hydrogen, the densities and refractive indices of higl purified toluene have been measured with the same apparat The data are in the following table, in which the bottom row c tains the differences between $[R_L]$ for benzyl fluoride and toluene:

		λ 6563.	λ 5893.	λ 5461.	λ 4861.	λ 4358.	λ 43
Benzyl fluoride	$n^{23\cdot3°}$	1·48481	1·48919	1·49294	1·50014	1·50927	1·50
$d_{4°}^{23\cdot3°}$ 1·02278	$[R_L]$	30·829	31·007	31·269	31·656	32·144	32·1
Toluene	$n^{23\cdot9°}$	1·48876	1·49331	1·49720	1·50454	1·51402	1·51
$d_{4°}^{23\cdot9°}$ 0·86140	$[R_L]$	30·833	31·077	31·285	31·676	32·177	32·19
		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Eisenlohr's (1910) values for the refraction constant of hydrogen being used, the contributions to the molecular refractions attributable to fluorine in benzyl fluoride are in the following table, in which Eisenlohr's values for the other halogens are included for comparison :

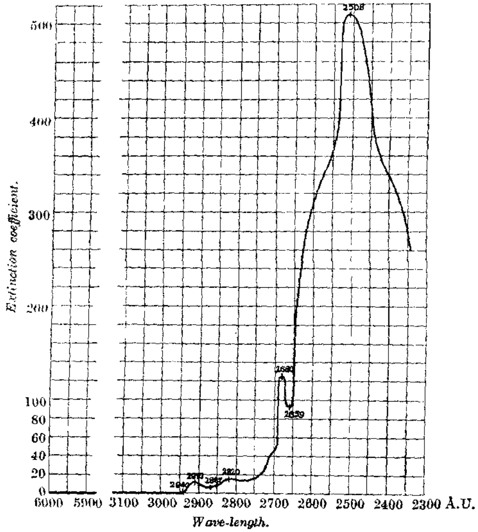
	H_α.	D.	H_β.	H_γ.	$H_\beta - H_\alpha$.	$H_\gamma - H_\alpha$.
F(BzF)	1·088	1·090	1·095	1·092	0·007	0·004
Cl	5·933	5·967	6·043	6·101	0·110	0·168
Br	8·803	8·865	8·999	9·152	0·196	0·349
I	13·757	13·900	14·224	14·521	0·467	0·764

It will be seen that fluorine has by far the lowest refraction values and that it differs sharply from the other halogens in contributing practically nothing to dispersion, and we conclude that amongst the four benzyl halides the halogen in benzyl fluoride exerts the *strongest positive field over the aromatic nucleus.* For *o*-, *m*-, and *p*-fluorotoluene Swarts (*J. Chim. phys.*, 1922, **20**, 30) obtained results which, when reduced in the same way, give − 0·034 (mean) for the contribution by fluorine to the dispersion (H_γ—H_α). For fluorobenzene the corresponding figure was − 0·045, and the marked contrast between these figures and that now derived (+ 0·004) for benzyl fluoride shows that the introduction of a fluorine atom into the aromatic nucleus causes a larger restraint on the electrons and hence a larger increase in the frequency governing dispersion than that produced by the entrance of a fluorine atom into the side chain.

Further evidence pointing in a similar direction was obtained by a study of the ultra-violet absorption of the substance, and the results are of interest in connexion with the parallelism which appears to subsist between the selective absorption of simply constituted aromatic compounds and their nuclear reactivity. It is known (Baly and Collie, J., 1903, **87**, 1332) that the conversion of aniline into a salt causes the selective absorption to be displaced in the direction of shorter wave-lengths, and this effect, manifestly connected with the increased electronic restraints produced by the positive charge, may be correlated with the inhibited nuclear reactivity and tendency to *m*-orientation of the salt. The opposite influence of a negative charge is displayed when phenol is converted into a salt, and the displacement of the selective absorption to a region of greater wave-lengths finds its counterpart in largely increased nuclear reactivity and very strong *op*-orientation. Spectrographic studies with benzene, toluene, ethylbenzene, and the three xylenes in alcoholic solution (Baly and Collie, *loc. cit.*) have shown that the introduction of alkyl groups into the aromatic nucleus displaces the absorption maximum towards the red, and quantitative data are available in the case of *p*-xylene (Henri, " Études de

Photochimie," 1919); the effect corresponds to *op*-orientation associated with increased nuclear reactivity (Ingold and Shaw's "Case I," J., 1927, 2918). If, however, the side-chain hydrogen atoms of toluene are replaced by atoms which attract electrons strongly, the circumstances of Ingold and Shaw's "Case I" pass into those of their "Case II," and continuously decreasing nuclear reactivity is associated with increasing *m*-orientation. Benzyl

Fig. 1.



fluoride, benzaldehyde, and benzoic acid represent progressive stages in this process, and it is therefore of interest to compare the positions and intensities of the principal ultra-violet absorption maxima of these substances with those of benzene and *p*-xylene. The curve representing the extinction coefficients for benzyl fluoride in *M*/*100*- to *M*/*1600*-ethyl-alcoholic solution is shown in the diagram, and a comparison of the wave-length of the maximum with those recorded by Henri (*loc. cit.*) for the other substances

shows that benzyl fluoride falls into place as a somewhat feebly *m*-orienting member of the series. The trend of the ϵ-values (minimum at benzene) suggests that electrical dissymmetry in the molecule favours photoelectronic excitation.

	p-Xylene.	Benzene.	Benzyl fluoride.	Benz-aldehyde.	Benzoic acid.
λ	2684	*2547*	2508	2,440	2,302
ϵ	750	*210*	508	16,260	44,700

It is not to be expected that the basis here indicated for the correlation of colour with constitution will be capable of a more general application until it has been considerably elaborated, and a more extended discussion of the effect of polar influences on colour must await further experimental studies.

The above reference to the *m*-orienting power of the fluoromethyl group is based on our observation that on nitration in acetic anhydride solution benzyl fluoride yields mononitro-derivatives in the following proportions: ortho- 28·1, meta- 17·5, para- 54·4%. Comparison of these figures with those which have been obtained by Miss F. R. Shaw in these laboratories for the nitration of benzyl chloride, namely, ortho- 32·0, meta- 15·5, para- 52·5%, shows that there is more *m*-substitution in the former case, and that therefore the electron-attraction (inductive + direct effects, $-I$ $-D$) of the halogen in benzyl fluoride is greater than in benzyl chloride.

According to Ingold and Vass (this vol., p. 417; see also Lapworth and Robinson, *Mem. Manchester Phil. Soc.*, 1928, **72**, No. 4) the direct effect is one of the main factors controlling the ortho/para ratio in aromatic substitution, and conversely this ratio, or the related ratio para/½ortho, may be taken to indicate the relative intensities of the external fields of the halogen atoms in the above cases, provided that the possibility of complications arising from steric hindrance is not disregarded. The ratios for benzyl fluoride and chloride are 3·89 and 3·28 respectively, showing that the direct effect of fluorine is stronger than that of chlorine, since steric hindrance should produce a difference in the opposite direction. This is confirmed by the halogenobenzene ratios (Holleman), namely, PhF 13·76, PhCl 4·64, PhBr 3·30, PhI 2·85, which indicate that the complete sequence is $D_F > D_{Cl} > D_{Br} > D_I$. It is natural that the ratios for the phenyl compounds should be greater than for the corresponding benzyl compounds, because not only will the field over the nucleus be stronger in the former case owing to the proximity of the halogen atom, but also the difference between the distances of the ortho- and para-positions from the directing atom will be relatively greater. The fact that the difference between the values for fluorobenzene and chlorobenzene is greater

than that between the values for benzyl fluoride and benzyl chloride can be similarly explained, and it may also be a contributing circumstance that in the phenyl compounds a tendency towards sharing additional electrons with the nucleus (residuum of the tautomeric effect $+T$) in the order Cl>F increases the disparity between the external fields produced by these atoms.

These considerations, combined with conclusions previously reached on other grounds (Ingold and Shaw, *loc. cit.*; Ingold and Vass, *loc. cit.*), show that, whereas in regard to the tautomeric effect the halogens are in the order I>Br>Cl>F, they stand in the reverse order with respect to both their inductive and direct effects, and one of the most interesting problems in the chemistry of the benzyl halides arises in connexion with the reconciliation of the above analysis of their nuclear reactivity with the available data relating to their side-chain transformations. According to Ingold and Rothstein (this vol., p. 1217) the side-chain substitutions of benzene derivatives are of four types, which, for the benzyl halides, may be exemplified by the reactions with (1) amines, water, and alcohols, (2) halogens (high temperatures), (3) reducing agents, (4) powerful alkalis. These types are divisible into two groups, since the mechanism of the reactions of which (2) is an example may be regarded as a variant of that of the reactions of category (1): the latter involve the ionisation $C_6H_5\cdot\overset{+}{C}H_2\}\overset{-}{X}$ (X = halogen). Similarly, reactions of type (4) proceed by a mechanism closely allied to that which obtains in class (3), and these reactions involve the opposite process $C_6H_5\cdot\overset{-}{C}H_2\}\overset{+}{X}$. Now, if the above considerations relating to the inductive and direct effects produced by halogens be taken as indicating the electrical states of these atoms, then the sequence F>Cl>Br>I should connote the order of negativity of halogen substituents in corresponding compounds, that is, the degree of pre-formation of the halide anions. It follows that the relative ease of reactions involving the separation of the halide anions should accord with the above sequence, and the facility of those which require the separation of a real or potential halous kation should follow the opposite order. There exists much evidence indicating that the latter statement corresponds to reality so far as concerns the three previously-known benzyl halides and we have shown that benzyl fluoride falls into the sequence, since, under conditions in which benzyl chloride is reduced [reaction (3)], the fluoride remains unaffected, and furthermore, the conversion of the fluoride into benzyl ethyl ether by treatment with sodium ethoxide [reaction (4)] is much more difficult to bring about than is the corresponding reaction of the chloride. On the other hand,

general experience shows that benzyl iodide and bromide are *more* reactive towards tertiary bases and acid hydrolytic and alcoholytic agents than is the chloride, and we have shown that benzyl fluoride reacts with trimethylamine and with ethyl alcohol much less readily than does benzyl chloride. Thus it appears that in reactions requiring the separation of a halide anion, the reactivities of the benzyl halides are in the opposite order to that which might be expected from a consideration of the influences of halogens on nuclear aromatic substitutions, and we are therefore compelled to suppose that the primary condition affecting the reactivity of the halogen substituents themselves is not so much the average or actual electrical condition of these atoms, but rather the extent to which they *are capable* of temporary electrical polarisation by the external fields of reagent molecules; * in other words, the fundamental condition is the magnitude of the restoring forces brought into play when the electrons of the carbon–halogen linking are displaced in either direction; or, again, the matter might be expressed in terms of energy relations, since the restoring force (f) referred to will be connected, through the integral $\int_0^\infty f dx$, to the critical energy increment of ionisation. It seems a reasonable assumption that the relative displaceability of the shared electrons of the four halogens in corresponding halides will run parallel with that of the unshared halogen electrons, and there is an accumulation of evidence that whilst the unshared electrons which combine most readily with a positive charge are those of iodine (example: formation of iodinium salts), the electrons of the outer shell of iodine are also those which are most easily displaced by a combining anion (example: hydrolysis of *p*-iodoxynitrobenzene). Combining this evidence with facts such as those underlying Fajan's theory of covalency formation and Sidgwick's theory of the production of higher groups of valency electrons, it is but a short step to the inference that the shared halogen electrons in corresponding halogenohydrocarbons are most easily displaced *in both directions* in the case of the iodo-derivative and least easily in the case of the fluoride. Thus the probable order of decreasing restoring forces is F, Cl, Br, I, and this is the sequence required to account for the observations referred to above relating to the side-chain reactivity of the benzyl halides.

One consequence of the assumption that it is the external molecular fields of adjacent reagent molecules which polarise the carbon–halogen linking sufficiently to lead to side-chain substitutions of benzyl halides is that reagents of many kinds, including

* This statement may be expected to apply with a considerable degree of generality to substituents in carbon compounds.

those which are employed for nuclear substitutions, must (since they will also possess external molecular fields) bring about similar, if smaller, temporary electron displacements in the side chain. Concerning the effect of these side-chain polarisations on the result of nuclear substitution, it will be obvious that everything must depend on their duration, and the fact that a change of reagent has little influence on the proportions of the nuclear substitution products (provided that covalency formation does not take place between the side chain and the reagent) shows that the duration of the side-chain polarisations must be small. Nevertheless we believe that the cause here indicated is one of the principal factors which contribute to the small differences which have been observed in the proportions of nuclear substitutions by different reagents, and we deduce that the nuclear substitution of an iodo-compound should be more sensitive to a change of reagent than that of the corresponding bromo-derivative, and so forth (I>Br>Cl>F). Thus the interesting distinction between the state of polarisation and the polarisability of the halogens and other substituents should be capable of independent investigation along these lines.

Experimental.

Preparation of Benzyl Fluoride.—Benzyl chloride (60 c.c.) and a 33% solution of trimethylamine in ethyl alcohol (120 c.c.) were mixed in an open flask at the ordinary temperature and the mixture was shaken and cooled externally as long as was necessary to prevent the temperature from rising above 40° (about 15 mins.). A further 60 c.c. of benzyl chloride and 120 c.c. of trimethylamine solution were then added and the action was regulated as before. The flask was thereafter closed with a drying tube, kept for 1 hour, and heated at 45° for several hours (usually over-night) to complete the reaction. About 2 l. of dry ether were added and the hygroscopic benzyltrimethylammonium chloride was rapidly collected, washed with ether, and dissolved in water. The solution was treated (stirring) with a suspension of excess of silver oxide and filtered. The combined filtrate and washings were neutralised with 20% hydrofluoric acid and evaporated on the steam-bath to a viscous syrup. A third of the syrup thus obtained was distilled in a water-pump vacuum from a water-bath until the crystals of benzyltrimethylammonium fluoride, at first transparent, had dried and become opaque through efflorescence, and then with a free flame (the better to control frothing), through an ice-water condenser, into 400 c.c. of 10% hydrochloric acid cooled below 0°, in which the benzyl fluoride collected as an oil. A tower containing a small amount of hydrochloric acid cooled below 0° served to scrub a

further small quantity of benzyl fluoride from the methyl fluoride which passed into the pump. After the remainder of the syrup had been similarly distilled in two portions into the same receiver, the oil in this and the scrubber was extracted with ether, and the extract washed three times with 10% hydrochloric acid and twice with aqueous sodium hydrogen carbonate, and dried with sodium sulphate. The residue which remained after removal of the ether gave (*a*) 4 g. of distillate, b. p. up to 69°/65 mm.; (*b*) 54 g., b. p. 69—71°/65—66 mm.; (*c*) 4 g., b. p. 71—77°/65—66 mm.; and (*d*) about 4 g. of a yellow, less volatile residue. Redistillation of fractions (*a*) and (*c*) augmented (*b*) to 60 g. The hydrochloric acid solution was evaporated to a paste, which was distilled with concentrated aqueous potassium hydroxide to expel the trimethylamine; this was dried, collected in alcohol, and used again. The *benzyldimethylamine which remained as an oil was also recovered for use in the following method.*

The recovered benzyldimethylamine was treated with the theoretical quantity of benzyl bromide, about half of which was introduced slowly with shaking and external cooling. Just before the mass became inconveniently viscous the remainder was added quickly, the reaction then proceeding rapidly to completion with a large evolution of heat. The crystalline dibenzyldimethylammonium bromide was, without purification, converted into the hydroxide and thence into the fluoride, which was decomposed by distillation as in the first method (yield, about 60%). The recovered bases consisted of benzyldimethylamine and dibenzylmethylamine. The former on treatment with benzyl bromide, and the latter on treatment with methyl iodide, yielded quaternary salts from which a further stock of dibenzyldimethylammonium fluoride, and thence of benzyl fluoride, was obtained.

Gram-molecular quantities of tribenzylamine and methyl iodide were kept in a sealed flask at 45° (in a thermostat) for 10 days. The sparingly soluble tribenzylmethylammonium iodide was finely ground and well-stirred for 16 hours with 4·5 l. of an aqueous suspension of silver oxide at 80—90°. The hydroxide was converted into the fluoride, which was decomposed in the usual way, yielding 35 g. of benzyl fluoride. Dibenzylmethylamine and some tribenzylamine were recovered and used again.

Physical properties. The *benzyl fluoride* (Found: C, 76·3; H, 6·3. C_7H_7F requires C, 76·4; H, 6·4%) prepared by these methods is a colourless mobile liquid, which does not fume in air and is not lachrymatory. On cooling, it sets to a mass of white needles, m. p. − 36° (uncorr.), and the b. p.'s observed during the preparation were 40—40·5°/14 mm., 55—56°/30—30·5 mm., 70—71°/

66 mm., 85—86°/118—119 mm., 100—100·5°/244—246 mm., 139—140°/ordinary pressure (all uncorr.). For more precise physical characterisation a sample boiling within a range of 1° was further purified by distillation, controlled by m. p. determinations. After the first distillation the m. p.'s were as follows : first, 20%, $-$ 36·5°; middle, 60%, $-$ 35·5°; last, 20%, $-$ 37·5°. The middle fraction, on redistillation, gave a head fraction, m. p. $-$ 35°, a main fraction, m. p. $-$ 35°, and a tail fraction, m. p. $-$ 36°. The main fraction on distillation gave only fractions having m. p. $-$ 35° (corr.). The b. p. was 139·8°/753 mm. (corr.), which corresponds to 139·9°/760 mm. (corr.) if the small correction to standard pressure is made by means of the approximate vapour-pressure observations recorded above. The purified sample was used for the determinations of density and refractive index recorded on p. 2250, and for tracing the curve of extinction coefficients shown in the diagram. The toluene required for the former observations was carefully purified by freezing. The absorption curve is plotted from about 50 comparison photographs taken with a polarisation-photometer by Bellingham and Stanley, Ltd., and a spectrometer giving a dispersion at the plate of 80 Å.U. per cm. at λ 2500.

Action of Sulphuric Acid, Hydrofluoric Acid, and Certain Kinds of Glass.—Benzyl fluoride readily loses hydrogen fluoride under certain conditions and passes into a hydrocarbon, or mixture of hydrocarbons $(C_7H_6)_x$. When the liquid is touched with a rod moistened with concentrated sulphuric acid, a violent reaction sets in and rapidly spreads throughout the mass, much heat being generated and hydrogen fluoride copiously evolved. The product is an opaque white glass. It is sparingly soluble in alcohol and moderately easily soluble in benzene; but it could neither be distilled nor crystallised. It contained not more than a trace of fluorine, and analysis indicated the empirical composition C_7H_6, although the molecular weight is undoubtedly high. A similar product is obtained when benzyl fluoride is left in contact with concentrated hydrofluoric acid in a platinum vessel, but hydrochloric and nitric acids do not appear to induce the decomposition.

An identical, or closely similar, product, also giving analytical results in accordance with the formula $(C_7H_6)_x$, is obtained when benzyl fluoride decomposes spontaneously in glass vessels. The reaction, which may develop with almost explosive violence, appears to commence at the glass surface. In the earlier experiments it frequently occurred during distillation, commencing in the side tube, with etching of the glass, and spreading backwards into the distilling flask. The action seems to be autocatalytic, and when the pure stable liquid is deliberately contaminated with a trace of

a decomposing specimen the whole decomposes even in platinum. The kind of glass is an important factor, and no losses have so far occurred when Jena glass vessels have been used for distillation. For storage, moulded bottles of uncertain history are to be avoided; the pure fluoride has, however, been kept for months without any sign of deterioration in Wood Bros.' flasks and Parkes' test-tubes.

Action of Potassium Carbonate.—Benzyl fluoride (11 g.) was boiled for 6 hours with 400 c.c. of 10% potassium carbonate solution; the product on distillation yielded 4·4 g. of recovered benzyl fluoride, b. p. 137—142°, 3·4 g. of benzyl alcohol, b. p. 200—208°, and an intermediate fraction containing both. Benzyl chloride (12·5 g.), treated similarly, yielded only benzyl alcohol.

Action of Zinc and Alcohol.—According to Tommasi (*Ber.*, 1874, 7, 826) benzyl chloride, on boiling with zinc dust and ethyl alcohol, is reduced to toluene. We have confirmed this, but find that benzyl ethyl ether is also formed. Benzyl fluoride (11 g.) on similar treatment yielded neither toluene nor benzyl ethyl ether in significant quantities, and over 90% was recovered unaltered.

Action of Alcoholic Trimethylamine.—Benzyl chloride readily reacts with 33% ethyl-alcoholic trimethylamine and combination is complete when a mixture of the theoretical quantities has been kept at about 45° for 3 hours. A mixture of benzyl fluoride and 33% alcoholic trimethylamine in the correct proportion was kept at 44° for 20 hours. The product, on being poured into water and extracted with ligroin, gave back 80% of the original benzyl fluoride, b. p. 138—140°. The aqueous solution was evaporated until it was neutral; the quaternary base was then precipitated as its picrate (m. p. and mixed m. p. with genuine benzyltrimethylammonium picrate, 169—170°). The yield was 5%, and since the picrate is very sparingly soluble, it is probable that this approximately represents the proportion of quaternary salt formed under the conditions used.

Action of Sodium Ethoxide.—Benzyl chloride and sodium ethoxide react quantitatively and immediately at the boiling point of alcohol. Benzyl fluoride (11 g.) was boiled for 1 hour with a solution of sodium ethoxide prepared from 2·3 g. of sodium and 24 g. of ethyl alcohol. The product yielded unaltered benzyl fluoride (3·1 g., b. p. 139—144°), benzyl ethyl ether (2·2 g., b. p. 185—190°), and an intermediate fraction which contained a considerable amount of benzyl fluoride (sulphuric acid test).

Nitration.—Freshly distilled, absolute nitric acid (6·3 g.), freed from nitrous acid, was slowly mixed with acetic anhydride (16 g.) at 5°. After warming the solution to 25°, benzyl fluoride (11·0 g.) was added. Nitration proceeded at a convenient velocity, between

25° and 30°, and was controlled by cooling the mixture to 25° as often as the temperature mounted to 30°. When this ceased to occur, the flask was placed in a thermostat at 25° for 6 hours, after which its contents were shaken with ice and water to destroy the acetic anhydride. The straw-coloured oil was extracted with benzene, washed six times with water, which removed a trace of yellow dye, and once with aqueous sodium hydrogen carbonate, and dried with sodium sulphate. The benzene and any excess of benzyl fluoride were removed at 40—50°/14 mm. by a slow stream of dry air, and the nitration product was distilled under about 0·1 mm.; only an insignificant residue remained. The distillate (Expt. 1) had $n_D^{25°}$ 1·5385 (Found: C, 54·3; H, 3·8. Calc.: C, 54·2; H, 3·8%). The last few drops, collected separately, had $n_D^{25°}$ 1·5390, proving the absence of dinitration products. The corresponding figures for the product of Expt. 2 were $n_D^{25°}$ 1·5382; C, 54·2; H, 3·9%: and for the last drops of the distillate, $n_D^{25°}$ 1·5388.

These products partly crystallised at 0° and appeared to be wholly solid at −33°. That obtained from Expt. 1 was filtered off at the temperature of ice (solid = A_1), again at that of liquid sulphur dioxide (solid = B_1), and again in an ice–salt mixture (solid = C_1; liquid = D_1). The product of Expt. 2 was similarly treated, the filtration at 0°, however, being omitted (fractions B_2, C_2, D_2). Fractions A_1, B_1, and B_2 remained solid at the ordinary temperature and on crystallisation from ether–ligroin below 0° yielded long, colourless needles, m. p. 38·5°, of pure *p-nitrobenzyl fluoride* (Found: C, 54·4; H, 3·9. $C_7H_6O_2NF$ requires C, 54·2; H, 3·8%), since oxidation with alkaline permanganate under the standard conditions described below yielded *p*-nitrobenzoic acid (m. p. 230—233° unpurified, mixed m. p. 233—234°). Fractions C_1 and D_1, which were liquid at the ordinary temperature, were drained on porcelain at the temperature of liquid ammonia (C_1' and D_1'); and fractions C_2 and D_2 were crystallised from ligroin containing a trace of ether at about −40°, whereby, as was shown by oxidation, the *o*-nitro-compound was concentrated in the former (C_2') and the *m*-derivative in the latter (D_2'), so that these isomerides, although they could not be completely purified, were obviously produced in significant quantities.

For the estimation of the isomerides the mixed mononitro-derivatives were converted into the nitrobenzoic acids, which were estimated by separation (Baker and Ingold, J., 1926, 2462) and also by Baker's adaptation (J., 1927, 565) of Holleman's solubility method. Both methods were again standardised by application to artificial mixtures. The method of oxidation was different from those formerly employed, which proved unsatisfactory; the new

method depended on the formation of nitrobenzyl alcohols which were rapidly oxidised with permanganate of low concentration. Conversions of about 90%, reproducible to 1%, were obtained, and deviations in the conversions of the individual isomerides were corrected for (Ingold, Ingold, and Shaw, J., 1927, 813).

The nitration product (Expt. 3: $n_D^{25°}$ 1·5387; C, 54·3; H, 3·9%) was boiled with 50 parts of 10% aqueous potassium carbonate, and an equal volume of the same solution containing 3% of potassium permanganate was added in 75 equal parts at such a rate as to keep pace with the decolorisation as exactly as possible. The acids were isolated in 89·4% yield in the usual way (*M* by titration, 167·2; benzoic acid by sublimation, nil), and on separation gave 55·0% of *p*-nitrobenzoic acid, m. p. 234—235° unpurified, mixed m. p. 235—236°, and 17·6% of *m*-nitrobenzoic acid, m. p. 133—137°, mixed m. p. 138—140°, the recorded yields being corrected for the solubility of the *p*-acid in chloroform and of the *m*-barium salt in water. The yield of crude *o*-acid, m. p. 130—140° (containing *m*-acid), brought the total recovery to 99·7%. For the determination of the *m*-isomeride (18·0%) by solubility it was necessary to extend the reference curve given by Baker (*loc. cit.*) and the following additional determinations were made:

Meta added (mg.)	70·1	107·1	133·9	162·3	164·9
Meta found (mg.)	74·7	125·0	168·7	190·8	191·8

Fraction C_1' oxidised under the standard conditions gave nitrobenzoic acids in 89·0% yield (*M* by titration, 166·7; benzoic acid, nil), which on separation yielded 42·3% of *p*-nitrobenzoic acid, m. p. 231—234°, mixed m. p. 234—235°. The proportion of *m*-acid was determined by the solubility method to be 2·7%. Fraction C_2' yielded 88·8% of mixed nitrobenzoic acids, which on separation gave 29·2% of *p*-nitrobenzoic acid; the proportion of *m*-nitrobenzoic acid, determined by solubility, was zero. Fraction D_1' gave 90·9% of mixed acids (*M*, 167·3; benzoic acid, nil), which on separation yielded 14·5% of *p*-nitrobenzoic acid, m. p. 230—232°, mixed m. p. 232—234°, and 47·8% of *m*-nitrobenzoic acid, m. p. 131—136°, mixed m. p. 136—139°; the figure 47·8% was also obtained by the solubility method. Fraction D_2' yielded 91·2% of mixed acids, which on separation gavo 8·0% of *p*-nitrobenzoic acid, m. p. 229—233°, mixed m. p. 230—234°; the proportion of *m*-nitrobenzoic acid was found by the solubility method to be 65·1%. *p*-Nitrobenzyl fluoride gave nitrobenzoic acid in 89·6, 90·0% yields. The mean conversions are calculated to be ortho 88·4%, meta 92·9%, para 89·8%, and hence the proportions of *o*-, *m*-, and *p*-nitrobenzyl fluorides are: ortho 27·9%, meta 17·1%, para 55·0% (separation), meta 17·5% (solubility). Expts. 4, 5,

and 6 were carried out in like manner and the results are included in the following table :

	Nitrobenzoic acids.				Nitrobenzyl fluorides.			
		Separation.		Solubility.	Separation.			Solubility.
Nitration No.	Conversion into acids (%).	Para (%).	Meta (%).	Meta (%).	Ortho (%).	Meta (%).	Para (%).	Meta (%).
3	89·4	55·0	17·6	18·0	27·9	17·1	55·0	17·5
4	89·5	54·0	18·2	18·1	28·4	17·6	54·0	17·5
5	89·0	54·1	17·9	18·4	28·4	17·4	54·2	17·9
6	90·1	54·5	17·5	17·9	28·5	17·0	54·5	17·5
				Mean	*28·3*	*17·3*	*54·4*	*17·6*

Distillation of o-, m-, *and* p-*Nitrobenzyltrimethylammonium Fluorides.*—*p*-Nitrobenzyltrimethylammonium fluoride, which was prepared from *p*-nitrobenzyl chloride and trimethylamine *via* the quaternary chloride and hydroxide, yielded a crystalline neutral distillate when a water-pump was used, and a solid, together with an oil which contained combined fluorine, when the distillation was conducted with an oil-pump-backed two-stage diffusion pump and a charcoal–liquid-air trap. In each case the solid proved to be *p*-nitrobenzaldehyde (Found : C, 55·8 ; H, 3·6. Calc. : C, 55·6 H, 3·3%). In the vacuum of the diffusion pump the *o*- and *m*-nitro salts gave oily distillates, from which aqueous semicarbazide acetat at once precipitated the semicarbazones of *o*- and *m*-nitroben aldehydes. In each case a very small amount of an oil containin fluorine was obtained by washing the crude semicarbazones with mixture of equal parts of ether and ligroin. Energetic decon position with charring occurred under all conditions and effecti control could not be maintained.

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CCXCIV.—*The Nature of the Alternating Effect Carbon Chains. Part XXIX. Further Expe ments bearing on the Problem of the Ortho-P Ratio in Aromatic Substitution.*

BY CHRISTOPHER KELK INGOLD and CHARLES CYRIL NORRI VASS.

IN a previous paper (this vol., p. 417) we developed the hypot that the principal polar orienting influence determining the o para ratio in aromatic substitution arises from the ext field of the substituent or substituents already present (effect, *D*), although steric inhibition and the occurrence of s

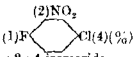
mechanisms may modify the situation in certain cases (*Ann. Reports*, 1926, **23**, 140). The experimental test then applied consisted in a comparison of the orienting effects of fluorine and chlorine in *p*-fluorochlorobenzene and *o*-fluorochlorobenzene; for the (negative) direct effects due to fluorine and chlorine are expected to be large and in the order F>Cl. It followed that, whereas in the *p*-compound, in which the direct effect assists the other polar factors, the relative control of nitration by the two halogens should follow the order Cl > F (Found: Direction by Cl/Direction by F = 72%/28%), in the case of the o-compound, in which the direct effect acts in opposition to the other influences, the order might be reversed (Found: Direction by Cl/Direction by F = 21%/79%).

Since the difference between the direct effects of fluorine and bromine should be greater than that between fluorine and chlorine, our attention was attracted (*loc. cit.*, footnote) to some recent papers by Hove (*Bull. Acad. roy. Belg.*, 1926, **12**, 801, 823; *Bull. Soc. chim. Belg.*, 1927, 361) in which it is shown that *p*-fluorobromobenzene on nitration in a large excess of sulphuric acid or in fuming sulphuric acid gave (although not in good yield) a product containing more than 40% of the *o*-fluoronitro-isomeride. In spite of the unsatisfactory yields this proportion appears to be definitely too high to be adequately accounted for on the lines indicated in our previous paper; but, having regard to the conditions employed by Hove in his nitrations, the considerations advanced by Ingold and Ingold (preceding paper) relating to the influence of media on orienting effects appeared to offer a possible basis for the explanation of Hove's result. According to this view, the external fields of reagent and solvent molecules are assumed to effect some degree of polarisation of the directing atom, and, if the *o*-*p*-substitution of the halogenobenzenes be regarded as evidence of the affinity of the unshared halogen electrons for a positive charge (tautomeric effect, + *T*), there can be little doubt that it would be the positive ends of dipolar solvent molecules which would be oriented towards the halogen. It need not be supposed, even when concentrated sulphuric acid is in contact with a halogen compound, that the formation of a real salt takes place, for Baker has shown in an independent series of observations (this vol., p. 1586) that it is possible experimentally to draw a clear distinction between the electrostriction of acids by weak bases and actual salt-formation involving co-ordination of the proton; at the same time he has proved that the polarising effect of the condition which may be described as *incipient* salt-formation is very considerable. Furthermore, turning again to the tautomeric effect in the substitution of the halogenobenzenes and to the indications afforded by Ingold

and Shaw's investigation of the relative velocity of these reactions (J., 1927, 2918), it is to be expected that the affinity of the unshared halogen electrons for a positive field will be in the order I>Br>Cl>F, and, *ceteris paribus*, that this order will therefore represent the effect of strong acids in polarising, and thus diminishing the *op*-orienting power of, halogen atoms. Finally, analogy with the nitration of acetanilide, in which the addition of sulphuric acid leads to the formation of appreciable quantities of the *m*-derivative, and also causes a marked rise in the ratio para/½ortho (Noelting and Collin, *Ber.*, 1884, **17**, 262; Holleman, Hartogs, and van der Linden, *Ber.*, 1911, **44**, 704), suggests that sulphuric acid produces particularly powerful medium-effects in substitution oriented by substituent atoms containing unshared valency electrons

Thus in Hove's experiments all the conditions calculated t produce an anomalous result are present, but it appeared impossib directly to test this view of the situation by further study of th nitration of *p*-fluorobromobenzene because Hove was unable t establish satisfactory conditions for this reaction in the absence c an excess of sulphuric acid. We have therefore sought for evidenc of the medium-effect in the analogous case of *p*-fluorochlorobenzer and have studied the effect of varying quantities of sulphuric an fuming sulphuric acids on the proportions in which the isomerid are formed. In the nitration of this substance the effect of t medium would be expected to be smaller than in *p*-fluorobrom benzene; nevertheless, it should be in the same direction and t addition of excess of acid should increase the proportion of t *o*-fluoronitro-compound (Cl>F).

That this is indeed the case is evident from the following figure

	Mols. H_2SO_4 per mol. HNO_3.					Mols. "free SO_3 per mo H_2SO_4.		
	0·00	0·67	0·86	3·00	6·00	0·33	0·64	[illegible]
	20·8	24·1	24·5	25·0	25·5	27·8	28·9	[illegible]
$\frac{1:2:4\text{-isomeride}}{1:3:4\text{-isomeride}} \times 100$	26·2	31·8	32·5	33·3	34·2	38·4	40·6	[illegible]

It will be seen that by the addition of sulphuric acid the portion of 1 : 2 : 4-compound relatively to its isomeride has l *increased* by 31%, and that the addition of fuming sulphuric caused an increase of 64%. These results not only furnish a suffi explanation of Hove's observations, but also suggest that in nitration of the monohalogenobenzenes the addition of sulpl acid should increase the ratio para/½ortho, and that this comb illustration of the operation of the direct effect and the polar

influence of solvent molecules should become increasingly marked with increasing atomic weight of the halogen. It is proposed to test these deductions.

EXPERIMENTAL.

p-*Fluorochlorobenzene and its Nitro-derivatives.*—*p*-Fluoroaniline (25 g.), prepared from *p*-fluoronitrobenzene (Ingold and Vass, *loc. cit.*), was diazotised at − 5° to 0° in solution in hydrochloric acid (175 c.c. of *d* 1·15; ice, 50 g.) with a concentrated solution of sodium nitrite. The solution was saturated with hydrogen chloride at 0°, treated with precipitated copper (20 g.) under reflux, and distilled in steam. The *p*-fluorochlorobenzene (yield, 66%), which was extracted with ether from the basified distillate and dried with phosphoric oxide, had b. p. 129—130° (compare Swarts, *Rec. trav. chim.*, 1915, **36**, 131).

2-Fluoro-5-chloronitrobenzene was prepared from *p*-fluoroaniline by nitration in sulphuric acid solution (Holleman, *Rec. trav. chim.*, 1905, **24**, 29) and subsequent replacement of the amino-group by chlorine (Swarts, *loc. cit.*). 5-Fluoro-2-chloronitrobenzene was prepared by an analogous series of reactions from *p*-fluoroacetanilide (Swarts, *loc. cit.*).

Nitration of p-*fluorochlorobenzene.* The nitration of this substance in nitric acid alone was studied by Swarts, whose quantitative results differ to some extent from those obtained by us. Swarts analysed his nitration product by two methods. First, ordinary thermal analysis indicated the presence of 27·75% of the *o*-fluoronitro-compound (Found by us, 20·8%); but a re-plot of Swarts's data connecting the f. p.'s of mixtures of the isomerides shows a marked deflexion in the neighbourhood of the composition of the nitration mixture. Since this deflexion depends only on one observation by Swarts, and since, furthermore, we have been quite unable to confirm it, it is probable that Swarts's figures require revision. Secondly, Swarts treated his nitration mixture with sodium methoxide under conditions in which, according to his observations, the *o*-fluoronitro-compound reacts completely and the *o*-chloronitro-compound is unaffected; the figure obtained by this method, namely, 27·78% of *o*-fluoronitro-compound, is in remarkably good agreement with the result of thermoanalysis. Our observations show, on the contrary, that neither under the conditions described by Swarts nor under any others that we have been able to discover is it possible to obtain a quantitative decomposition of one isomeride and a complete absence of any decomposition of the other; *e.g.*, under the conditions described by Swarts, 5-fluoro-2-chloronitrobenzene underwent hydrolysis to the

extent of 11·6—12·3% (see Table IV). From these observations it appears that it is impossible to analyse the nitration product by this method, and that the agreement obtained by Swarts was fortuitous.

The conditions under which the various nitrations were carried out are recorded in Table I. In all experiments the temperature was − 15° to −10°. The isolation of the product was effected by the method previously described for *o*-fluorochlorobenzene (Ingold and Vass, *loc. cit.*). The synthesised isomerides were isolated and purified by a similar process. The freezing points recorded in Tables I, II, and III are uncorrected, but were determined under identical conditions with the same apparatus. In order to control possible changes of composition during isolation, the material, after the f.-p. determination, was redissolved in nitric acid and the isolation repeated, with the result that the f. p. remained unaltered to within 0·1°. Furthermore, as a check on the binary character of the nitration products, some of these were mixed with known proportions of the pure isomerides and the f. p.'s of the mixtures were compared with the f. p.–composition curve.

TABLE I.

Thermal Analysis of Nitration Products.

Expt.	Yield of nitration product (%).	Yield of 4-chloro-2-nitrophenol (%).	HNO_3 (mols. excess).	H_2SO_4 (mols.).	"Free" SO_3 (mols.).	F. p.	2-Fluoro-5-chloro-nitro-benzene (%).
1, 2	92	1·4	3·5	—	—	26·8°	20·7
3, 4	94	2·6	2·2	—	—	26·6	21·0
8	95	0·4	1·7	1·8	—	25·0	24·1
7	95	0·5	2·5	3·0	—	24·85	24·5
5	99	—	—	3·0	—	24·6	25·0
6	100	—	—	6·0	—	24·3	25·5
9	100	—	—	2·6	0·85	23·2	27·6
10	90 *	—	—	5·2	1·7	23·0	28·0
14	100	—	—	3·3	2·1	22·6	28·9
11, 12, 13	100	—	—	1·5	2·8	22·0	30·0

* Accidental mechanical loss.

TABLE II.

Freezing Points of Mixtures of 2-Fluoro-5-chloronitrobenzene (p) and 5-Fluoro-2-chloronitrobenzene.

p (%)	0·00	19·80	22·29	22·78	24·52	24·79	26·21
F. p.	35·90°	27·30°	26·00°	26·20°	24·70°	24·60°	24·20°
p (%)	27·16	28·53	29·26	32·53	33·65	35·77	37·94
F. p.	23·90°	22·50°	22·20°	20·80°	19·00°	19·00°	18·00°
p (%)	38·14	42·80	61·47	89·40	100·00		
F. p.	16·10°	13·20°	1·80°	3·00°	8·00°		

TABLE III,

Illustrating Binary Character of Nitration Mixtures.

= composition from f.-p. curve. Percentage of 2-fluoro-5-chloronitrobenzene.

= new compositions calc. from original f. p. and weights of isomerides added. Percentage of 2-fluoro-5-chloronitrobenzene.

Expt.	Original f. p.	*a*.	*b*.	New f. p. found.	New f. p. from curve.
2	26·8°	20·7	17·8	28·1°	28·2°
6	24·3	25·5	29·2	22·5	22·5
,,	,,	,,	36·3	18·3	18·6

TABLE IV.

)ecomposition of the Fluorochloronitrobenzenes with Methyl-alcoholic Sodium Methoxide.

Isomeride or mixture.	Weight (g.).	Temp.	Conditions.	Total halide ions formed.*	Chloride ions formed.†
-Fluoro-2-chloronitrobenzene	5·8662	25°	Swarts‡	12·13	Not
,, ,,	3·0196	,,	,,	11·57	deter-
,, ,,	4·4123	,,	,,	12·30	mined
-Fluoro-5-chloronitrobenzene	4·2242	,,	,,	100·3	0·0
litration product. Expt. 3	5·1744	,,	,,	33·16	Not
,, ,, Expt. 4	3·7192	,,	,,	36·11	deter-
,, ,, Expt. 2	2·7317	,,	,,	35·8	mined
-Fluoro-2-chloronitrobenzene	0·2655	100	Ingold ‡	Not	85·6
-Fluoro-5-chloronitrobenzene	0·2011	,,	and	deter-	5·66
litration product. Expt. 2	0·2386	,,	Vass	mined	70·5

* Measured by loss in alkalinity. † Directly estimated.

‡ *Loc. cit.*

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)CXCV.—*Electrometric Titration Curves of Dibasic Acids. Part II. β-Substituted Glutaric Acids.*

By RICHARD GANE and CHRISTOPHER KELK INGOLD.

N Part I (this vol., p. 1594) we described a preliminary examination ıto the possibility of obtaining approximate measurements of he distance between the carboxyl groups of dibasic acids by tilising hydrogen-ion activity determinations, during neutralisation rith a strong base, in conjunction with Bjerrum's theory respecting he effect of the external field of a pole on the degree of dissociation f another ionising centre situated in the same molecule. It was hown that the results obtained by this method for the distances

between the carboxyl groups of normal dibasic acids, are subject to various disturbances, of which probably the most important are the following: (1) the influence of solvation and electrostriction, which, although it interferes with quantitative accuracy, should not, and apparently does not, alter the order of a given series of related substances in respect of the dimension considered: (2) the effect of internally propagated polar influences, which gives rise to larger anomalies the shorter the carbon chain between the carboxyl groups. It was found, furthermore, that the disturbances attributable to internal influences, although large in malonic acid and considerable in succinic acid, became small in glutaric acid and its higher normal homologues, and it was therefore decided to examine a series of substituted glutaric acids in order to ascertain whether the hypothesis of valency deflexion, which has hitherto been successful mainly in explaining chemical relationships, would receive support from physical measurements.*

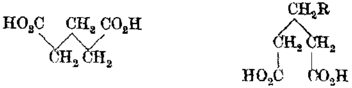
We have examined glutaric acid, two β-alkylglutaric acids, three ββ-dialkylglutaric acids, and three related ring compounds. The values of the first and second electrometric dissociation constants and the calculated value of the apparent distance r (in Ångström units) between the carboxyl groups are shown in the following table:

Substance.	k_1.	k_2.	r.
Glutaric acid	$4·60 \times 10^{-5}$	$5·34 \times 10^{-6}$	9·22
β-Methylglutaric acid	$5·77 \times 10^{-5}$	$6·28 \times 10^{-7}$	2·27
β-*n*-Propylglutaric acid	$4·97 \times 10^{-5}$	$4·32 \times 10^{-7}$	2·12
ββ-Dimethylglutaric acid	$2·03 \times 10^{-4}$	$5·51 \times 10^{-7}$	1·57
ββ-Diethylglutaric acid	$3·40 \times 10^{-4}$	$7·85 \times 10^{-8}$	1·02
ββ-Di-*n*-propylglutaric acid	$2·03 \times 10^{-4}$	$5·42 \times 10^{-8}$	1·01
*cyclo*Pentane-1 : 1-diacetic acid	$1·68 \times 10^{-4}$	$2·63 \times 10^{-7}$	1·40
*cyclo*Hexane-1 : 1-diacetic acid	$3·36 \times 10^{-4}$	$1·02 \times 10^{-7}$	1·04
*cyclo*Heptane-1 : 1-diacetic acid	$2·78 \times 10^{-4}$	$1·09 \times 10^{-7}$	1·10

The most remarkable feature presented by these data is the fact that the value for r for glutaric acid is so very much greater than for any of the substituted acids. In Part I, it was shown that the normal (unsubstituted) dibasic acids tend to a straight (zig-zag), and not a coiled, configuration, since the apparent distance between the carboxyl groups increases regularly by 1·73 Å.U. for each methylene group in this series of homologues. The value 9·2 Å.U. for glutaric acid is in keeping with this conception, and there appears to be no other way of explaining the much smaller values given by

* Spiers and Thorpe (*J.*, 1925, **127**, 538) pointed out the close parallelism between the first dissociation constants (conductivity) of substituted glutaric acids and the tendency to ring-closure of corresponding derivatives, and this, therefore, is the first indication that valency-deflexion may manifest itself in physical properties.

the substitution products than to suppose that the presence of a β-substituent causes the molecule to assume the coiled configuration:



Apart from this unexpected result, the data are in general agreement with the valency-deflexion hypothesis in regard to both the sequence of the compounds and the relative magnitude of the differences in respect of the property under discussion. Thus the value for the β-propyl acid is less than that for the β-methyl derivative; the value for β-ethylglutaric acid was not determined, but it would be expected to approximate closely to the figure for the propyl compound. The distance for the *gem*-dimethyl acid is, however, considerably less than for either of the mono-substituted acids, and this is in conformity both with the spatial theory of valency-deflexion and with the chemical evidence relating to these examples which has been adduced in support of it (Ingold, J., 1921, **119**, 305; 1922, **121**, 2676). Again, both on theoretical grounds and also by analogy with chemical evidence (Deshapande and Thorpe, J., 1922, **121**, 1430; Bains and Thorpe, 1923, **123**, 1206), it would be expected that the distance for the ββ-diethyl acid should be substantially less than for the dimethyl compound, whilst the value for the ββ-di-*n*-propyl derivative should be only very slightly less than for its diethyl analogue. It will be seen that the measurements bear out both these expectations, although the small recorded difference (0·01 Å.U.) between the distances for the diethyl and dipropyl acids cannot be regarded as possessing quantitative significance.

According to the elementary form of the deflexion hypothesis, the distance *r* for *cyclo*pentanediacetic acid would be expected to be slightly greater than that for the *gem*-dimethyl analogue; chemical evidence, however, indicates that it might be slightly smaller (Becker and Thorpe, J., 1920, **117**, 1579), and it would be possible to reconcile this discrepancy by means of a minor modification of the theory, provided that the value for the *cyclo*pentane acid is definitely greater than that for its open-chain analogue having the same number of carbon atoms, *viz.*, the diethyl acid. The data now recorded show that the distance for the *cyclo*pentane acid is actually slightly less than that for the *gem*-dimethyl acid, in agreement with the chemical indications, and is considerably greater than that for the *gem*-diethyl acid as theory requires. The distance for the

*cyclo*hexane acid should, of course, be less than for either the *gem*-dimethyl or the *cyclo*pentane acid (Beesley, Ingold, and Thorpe, J., 1915, **107**, 1080), and the measurements illustrate this. Finally, according to Baker and Ingold's conception (J., 1923, **123**, 122) of the influence of large rings in producing valency-deflexion, the value for *cyclo*heptanediacetic acid should be between the values for the *cyclo*hexane and *cyclo*pentane acids, since the maximum deflexion occurs with *cyclo*hexane. This also is shown by the data now submitted, and corresponds with the evidence already obtained by the study of *spiro*-compounds (*idem, ibid.*; Baker, J., 1925, **127**, 1678).

In conclusion, then, it may be stated that the measurements here recorded justify the suggestion of Ingold and Thorpe (this vol., p. 1318) that a study of the dissociation constants of β-substituted glutaric acids would confirm all the main features of the hypothesis of valency-deflexion by means of which for some 13 years past they have interpreted chemical relationships. Furthermore, it will be seen that where unexpected chemical observations have suggested modifications of the original hypothesis, the physical measurements confirm the modifications.

EXPERIMENTAL.

The substituted glutaric acids were prepared by known methods and carefully purified * by repeated crystallisations before use. The hydrogen potential measurements were carried out and standardised and the results calculated exactly as described in Part I, and in this connexion we have again to thank Messrs. W. R. Atkin and F. C. Thompson for the loan of their apparatus. The temperature was in all cases 25°.

β-*Methylglutaric acid.* Original concentration 0·00675*M*; NaOH equivalent to 0·002567 g. Na˙/c.c.; equivalent titre 18·15 c.c.

Titre.	p_H.	Titre.	p_H.	Titre.	p_H.	Titre.	p_H.
0·00	3·253	4·97	4·199	11·53	5·029	16·65	5·929
0·34	3·361	5·88	4·333	12·56	5·164	17·24	6·169
0·77	3·442	6·76	4·446	13·50	5·291	17·59	6·392
1·14	3·531	7·62	4·550	14·40	5·432	17·89	6·754
1·71	3·658	8·55	4·664	14·99	5·533	18·03	7·083
2·28	3·773	9·50	4·772	15·53	5·636	18·08	7·269
3·06	3·913	10·52	4·905	16·09	5·767	18·10	7·684
3·99	4·058						

* Since acids, which appear pure as judged by ordinary standards, may contain a non-acidic impurity which "poisons" the electrodes, causing instability in the null-points, it is desirable to include washing the sodium salts with acetone in the scheme of purification.

β-n-*Propylglutaric acid.* Original concentration 0·004768*M*; NaOH equivalent to 0·002567 g. Na˙/c.c.; equivalent titre 12·82 c.c.

Titre.	p_H.	Titre.	p_H.	Titre.	p_H.	Titre.	p_H.
0·00	3·331	2·98	4·188	7·01	4·947	10·70	5·713
0·31	3·450	3·61	4·320	7·60	5·056	11·24	5·875
0·74	3·599	4·24	4·440	8·24	5·177	11·65	6·037
1·26	3·764	5·08	4·598	8·88	5·301	12·02	6·223
1·82	3·920	5·63	4·696	9·51	5·430	12·42	6·535
2·46	4·071	6·31	4·821	10·10	5·557	12·66	6·912

ββ-*Dimethylglutaric acid.* Original concentration 0·007995*M*; NaOH equivalent to 0·002567 g. Na˙/c.c.; equivalent titre 21·50 c.c.

0·00	2·914	4·30	3·573	9·48	4·527	16·02	6·245
0·20	2·962	4·76	3·642	10·00	4·697	17·00	6·393
0·62	3·026	5·28	3·713	10·49	4·892	18·00	6·559
1·20	3·116	5·90	3·802	10·97	5·095	19·02	6·767
1·77	3·209	6·51	3·901	11·50	5·299	20·00	7·033
2·40	3·299	7·10	4·002	11·98	5·457	21·23	7·827
2·79	3·355	7·78	4·120	12·98	5·708	21·27	7·910
3·30	3·432	8·50	4·266	14·01	5·912	21·60	9·562
3·80	3·503	8·96	4·381	15·00	6·083	21·63	9·731

ββ-*Diethylglutaric acid.* Original concentration 0·00545*M*; NaOH equivalent to 0·002567 g. Na˙/c.c.; equivalent titre 14·65 c.c.

0·00	2·942	3·82	3·578	7·20	5·090	10·58	7·017
0·30	2·985	4·30	3·675	7·40	5·443	11·44	7·210
0·98	3·084	4·89	3·810	7·60	5·748	12·19	7·406
1·50	3·167	5·41	3·950	8·02	6·139	12·99	7·626
1·85	3·225	5·81	4·076	8·42	6·362	13·62	7·878
2·28	3·294	6·22	4·233	9·00	6·587	14·54	8·758
2·80	3·384	6·59	4·435	9·80	6·819	14·86	9·850
3·42	3·498	6·95	4·743				

ββ-*Dipropylgluratic acid.* Original concentration 0·0005455*M*; NaOH equivalent to 0·0003671 g. Na˙/c.c.; equivalent titre 10·25 c.c.

0·00	3·612	3·00	4·106	4·80	5·095	6·90	7·001
0·31	3·664	3·51	4·255	5·42	6·139	7·43	7·169
0·75	3·713	4·00	4·441	5·62	6·359	8·02	7·369
1·30	3·790	4·40	4·677	5·95	6·592	9·76	8·100
1·89	3·884	4·60	4·839	6·40	6·821	10·74	9·317
2·51	4·005						

cyclo*Pentane*-1 : 1-*diacetic acid.* Original conc. 0·003421*M*; NaOH equivalent to 0·002567 g. Na˙/c.c.; equivalent titre 9·20 c.c.

0·00	3·186	3·01	4·091	5·40	5·961	7·51	6·824
0·25	3·239	3·30	4·211	5·62	6·077	7·82	6·945
1·50	3·602	3·60	4·358	5·92	6·217	8·10	7·084
1·79	3·688	3·90	4·531	6·22	6·344	8·40	7·246
2·10	3·783	4·20	4·782	6·53	6·461	8·98	7·852
2·40	3·880	4·40	4·992	6·86	6·582	9·35	9·696
2·71	3·982	4·60	5·249	7·20	6·707		

cyclo*Hexane*-1 : 1-*diacetic acid*. Original conc. 0·002232*M* ; NaOH equivalent to 0·002567 g. Na˙/c.c. ; equivalent titre 6·00 c.c.

Titre.	p_H.	Titre.	p_H.	Titre.	p_H.	Titre.	p_H.
0·25	3·200	1·78	3·798	3·43	6·239	5·88	8·311
0·60	3·327	1·96	3·901	3·80	6·548	6·02	9·059
0·90	3·429	2·25	4·088	4·10	6·747	6·16	9·798
1·30	3·584	3·17	5·863	4·39	6·921		

cyclo*Heptane*-1 : 1-*diacetic acid*. Original conc. 0·000733*M* ; NaOH equivalent to 0·0003671 g. Na˙/c.c. ; equivalent titre 13·8 c.c

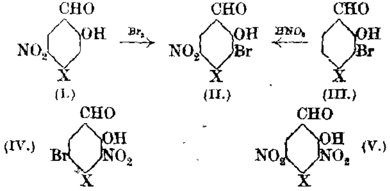
0·00	3·455	4·03	3·979	7·68	6·122	11·50	7·275
0·31	3·502	4·61	4·094	8·10	6·324	12·00	7·386
0·68	3·546	5·20	4·247	8·62	6·552	12·52	7·530
1·23	3·602	5·82	4·474	9·22	6·729	12·99	7·674
1·86	3·672	6·30	4·747	9·68	6·854	13·94	8·029
2·28	3·722	6·75	5·010	10·31	7·000	14·34	8·300
2·82	3·790	7·00	5·570	10·93	7·144	14·52	8·445
3·40	3·873	7·32	5·892				

The University, Leeds. [*Received, June 13th*, 1928.]

CCXCVI.—*Nitration of 4-Halogeno-2-hydroxy- an 2-Halogeno-4-hydroxy-benzaldehydes.*

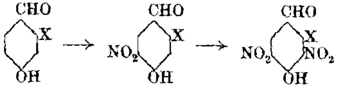
By Herbert Henry Hodgson and Thomas Alfred Jenkinsc

The mononitration of the 4-halogenosalicylaldehydes, hitherto ı studied, produces only one series of nitro-derivatives, althoı dinitration is readily accomplished. The first nitro-group appear enter position 5, since bromination of the products (I) affords compounds (II) obtained by nitrating the 3-bromo-4-haloge salicylaldehydes (III). Since, however, the 4-halogenomononi 2-hydroxybenzaldehydes were sufficiently volatile in steam indicate that nitration might have taken place in the 3-position, products (IV) were prepared for comparison. The sodium salt (I) and (II) are yellow, whereas those of (IV) are bright indicating para- and ortho-nitrophenolic structures respecti Dinitration of the 4-halogenosalicylaldehydes gives products w for the same reasons, must be 3 : 5-dinitro-derivatives (V).



(I.) (II.) (III.) (IV.) (V.)

The 2-halogeno-4-hydroxybenzaldehydes are similarly converted into the 5-nitro- and 3 : 5-dinitro-compounds :



The brown colours produced by alkalis on the phenylhydrazones of certain of these substituted *m*-nitrobenzaldehydes are in accord with the observations of Chattaway and Clemo (J., 1923, **123**, 3043).

EXPERIMENTAL.

Nitration of 4-Chloro-2-hydroxybenzaldehyde.—(*a*) *Mononitration.* 4-Chloro-2-hydroxybenzaldehyde (2 g.), dissolved in glacial acetic acid (5 c.c.), was nitrated at 18° by addition of fuming nitric acid (0·5 c.c.) during 3 minutes, and kept for 8 hours at 60° with stirring. On pouring into water, a yellow, oily liquid separated which was steam-distilled, two fractions (150 c.c. each) being collected. The first contained unchanged aldehyde (0·2 g.) with a little nitro-product. From the second fraction (0·2 g.), 4-*chloro-5-nitro-2-hydroxybenzaldehyde* (0·3 g.) was obtained, which crystallised from alcohol in small pale yellow needles, m. p. 116° (Found : Cl, 17·6. $C_7H_4O_4NCl$ requires Cl, 17·6%), sparingly soluble in water and light petroleum, but readily soluble in the usual solvents; the product does not reduce ammoniacal silver nitrate or Fehling's solution or react with bromine water. The *phenylhydrazone* crystallises from alcohol in small light orange-yellow needles, m. p. 188° (decomp.) (Found : Cl, 12·0. $C_{13}H_{10}O_3N_3Cl$ requires Cl, 12·2%), which give golden-brown solutions with caustic alkalis. The p-*nitrophenylhydrazone* crystallises from alcohol or glacial acetic acid in bright yellow micro-needles, m. p. 294° (decomp.) (Found : Cl, 10·5. $C_{13}H_9O_5N_4Cl$ requires Cl, 10·5%), which give cherry-red colours with concentrated alkalis, turning bluer on dilution. The *semicarbazone* crystallises from dilute acetic acid in very pale yellow micro-needles, which decompose above 300° (Found : Cl, 13·5. $C_8H_7O_4N_4Cl$ requires Cl, 13·7%).

(*b*) *Dinitration.* The aldehyde (0·75 g.) dissolved in glacial acetic acid (8 c.c.) is added all at once to nitric acid (8 c.c.; 91%) and, after the violent reaction has abated, the mixture is warmed at 100° for 5 minutes, kept for 15 minutes, poured into water, and steam-distilled to remove volatile mononitro-product. 4-*Chloro-3 : 5-dinitro-2-hydroxybenzaldehyde* (1 g.) crystallises from water in slender, pale golden-yellow needles, m. p. 153° (Found : Cl, 14·5.

$C_7H_3O_6N_2Cl$ requires Cl, 14·4%), which neither reduce Fehling's solution nor give a precipitate with bromine water. The *phenylhydrazone* crystallised from alcohol in light brown micro-crystals, m. p. 219° (Found: Cl, 10·3. $C_{13}H_9O_5N_4Cl$ requires Cl, 10·55%), and gives a golden-brown colour with alkalis. The p-*nitrophenylhydrazone* crystallises from dilute acetic acid in light brown micro-crystals, m. p. 286° (decomp.) (Found: Cl, 9·1. $C_{13}H_8O_7N_5Cl$ requires Cl, 9·3%), and with aqueous and alcoholic sodium hydroxide gives a cherry-red colour which turns a bluer shade on dilution. The *semicarbazone* separates from dilute acetic acid in light yellow micro-crystals, m. p. 225° (decomp.) (Found: Cl, 11·5. $C_8H_6O_6N_5Cl$ requires Cl, 11·7%).

Nitration of 2-Chloro-4-hydroxybenzaldehyde.—(*a*) *Mononitration.* The aldehyde (3 g.), dissolved in glacial acetic acid (15 c.c.), was nitrated by the gradual addition of nitric acid (3 g.; 63%), the mixture then being kept at 35—40° for 2 hours. The 2-*chloro*-5-*nitro*-4-*hydroxybenzaldehyde* was removed by steam-distillation and crystallised from alcohol in colourless needles, m. p. 125° (Found: Cl, 17·6. $C_7H_4O_4NCl$ requires Cl, 17·6%), only slightly soluble in water and less soluble in the usual solvents than the initial aldehyde. The *phenylhydrazone* crystallised from alcohol in silky, dark purple needles, m. p. 166° (slight decomp.) (Found: Cl, 12·1%), which gave no colour with aqueous but a red with alcoholic alkalis. The p-*nitrophenylhydrazone* crystallised from glacial acetic acid in small, silky, deep orange needles, m. p. 266° (decomp.) (Found: Cl, 10·4%), which gave a violet-red colour with aqueous and alcoholic alkalis, turning bluer on dilution. The *semicarbazone* crystallised from dilute acetic acid in light orange micro-needles, m. p. 266° (decomp.) (Found: Cl, 13·6%).

(*b*) *Dinitration.* The aldehyde (3 g.), dissolved in glacial acetic acid (10—15 c.c.), was added gradually (10 minutes) to nitric acid (6 g.; 63%); the mixture was kept at 60° for 2 hours, poured into water, and steam-distilled. The non-volatile 2-*chloro*-3 : 5-*dinitro*-4-*hydroxybenzaldehyde* crystallised from water in pale yellow, massive, prismatic crystals, m. p. 93° (Found: Cl, 14·3%), sparingly soluble in cold but readily soluble in hot water. The *phenylhydrazone* crystallised from alcohol in small, lustrous, brownish-purple needles, m. p. 210° (decomp.) (Found: Cl, 10·4%), which give a red colour with aqueous-alcoholic alkalis. The p-*nitrophenylhydrazone* crystallised from dilute acetic acid in reddish-brown micro-needles, m. p. 267° (decomp.) (Found: Cl, 9·1%), which gave a violet-red colour with alkalis, changing to a fine violet on dilution. The *semicarbazone* crystallised from dilute acetic acid in light brown micro-needles, m. p. 192° (decomp.) (Found: Cl, 11·5%).

Reimer–Tiemann Reaction with 3-Chloro-2-bromo- and 2 : 3-Dibromo-phenols.—The procedure employed was that in the authors' previous paper (J., 1927, 1740), but the yields were only moderate. *4-Chloro-3-bromo-2-hydroxybenzaldehyde* forms colourless needles, m. p. 124° (0·1000 g. gave 0·1390 g. of AgX.* Calc.: 0·1407 g.), having a faint sweet odour, slowly volatile in steam, sparingly soluble in water but readily soluble in the usual organic solvents; the *phenylhydrazone*, colourless needles, m. p. 204° (0·1000 g. gave 0·1010 g. AgX. Calc.: 0·1018 g.), gave a pale yellow solution with aqueous-alcoholic alkalis; the p-*nitrophenylhydrazone*, orange micro-needles, m. p. 298° (decomp.), gave a ruby-red colour with aqueous alkalis. *3-Chloro-2-bromo-4-hydroxybenzaldehyde*, colourless needles, m. p. 177° (0·1000 g. gave 0·1415 g. AgX. Calc.: 0·1407 g.), is very slowly volatile in steam and resembles its isomeride in solubilities; the p-*nitrophenylhydrazone*, dark crimson micro-needles, m. p. 253° (decomp.) (0·1000 g. gave 0·0900 g. AgX. Calc.: 0·0895 g.), gave a deep purplish-red colour with aqueous alkalis. 3 : *4-Dibromo-2-hydroxybenzaldehyde* forms colourless needles, m. p. 129° (Found: Br, 56·9. $C_7H_4O_2Br_2$ requires Br, 57·1%), volatile in steam, and having a faint sweet odour. The p-*nitrophenylhydrazone*, orange micro-needles, decomp. above 220° (Found: Br, 38·3. $C_{13}H_9O_3N_3Br_2$ requires Br, 38·55%), gives a ruby-red colour with alkalis, becoming bluer on dilution.

2 : *3-Dibromo-4-hydroxybenzaldehyde*, colourless needles, m. p. 192° (Found: Br, 57·0%), is only very slightly volatile in steam and odourless. The p-*nitrophenylhydrazone*, vermilion-red micro-needles, m. p. 254° (decomp.) (Found: Br, 38·3%), gave a deep red colour with aqueous alkalis.

Nitration of 4-Chloro-3-bromo-2-hydroxybenzaldehyde.—The aldehyde (1·5 g.), dissolved in glacial acetic acid (5 c.c.), was nitrated at 60—65° during 2 hours with nitric acid (0·5 g.; *d* 1·5). The *4-chloro-3-bromo-5-nitro-2-hydroxybenzaldehyde* crystallised from alcohol in yellow prisms, m. p. 137° (Found: Cl + Br, 40·8. Calc.: 41·2%). The *phenylhydrazone* crystallised from alcohol in bright yellow needles, m. p. 229° (decomp.) (Found: Cl + Br, 31·3. Calc.: 31·2%), and gave brown colours with alkalis.

Bromination of 4-Chloro-5-nitro-2-hydroxybenzaldehyde.—The aldehyde (0·5 g.) in glacial acetic acid (2 c.c.) was treated with 3 c.c. of a solution of bromine (2 g.) in the same solvent (10 c.c.), the mixture warmed for 5 minutes on the water-bath, diluted with water until the slight turbidity just disappeared on heating, and allowed to cool slowly; 4-chloro-3-bromo-5-nitro-2-hydroxybenzaldehyde separated in yellow prisms, m. p. 137° (Found: Cl + Br, 40·9%),

* AgX = mixed silver halides.

unaltered when mixed with foregoing product. The yellow *sodium* salt was sparingly soluble in aqueous sodium carbonate. The *phenylhydrazone* crystallised from alcohol in bright yellow needles m. p. 229° (decomp.) (Found : Cl + Br, 31·4%); a mixed m. p with the corresponding product above indicated identity.

Preparation of 4-Chloro-5-bromo-2-hydroxybenzaldehyde.—To *m*-chlorophenol (23 g.), dissolved in chloroform (70 c.c.), bromine (9 c.c.) dissolved in chloroform (60 c.c.) was gradually added with shaking. After the free bromine had disappeared, the mixture was refluxed with 20% aqueous sodium hydroxide (200 c.c.) for 4 hours, the chloroform removed by means of steam, the mixture acidified, and again steam-distilled; *4-chloro-5-bromo-2-hydroxybenzaldehyde* readily passed over: colourless needles, m. p. 125° (0·0838 g. gave 0·1181 g. AgX. Calc.: 0·1180 g.), from dilute acetic acid. The *phenylhydrazone* crystallised from alcohol in colourless needles, m. p. 200° (Found : Cl + Br, 35·2. Calc.: 35·5%). The p-*nitrophenylhydrazone* crystallised from glacial acetic acid in small, light brown needles, m. p. 280° (decomp.) (Found : Cl + Br, 30·9. Calc.: 31·2%), which gave a blue cherry-red colour with aqueous and alcoholic alkalis.

Nitration of 4-Chloro-5-bromo-2-hydroxybenzaldehyde.—The aldehyde (2 g.) was dissolved in warm acetic anhydride (2 c.c.) and obtained as a paste of fine crystals by chilling; it was then treated gradually with diacetylorthonitric acid (2 c.c.), maintained at 50° for 15 minutes, and kept over-night; *4-chloro-5-bromo-3-nitro-2-hydroxybenzaldehyde* separated, and crystallised from alcohol in large, pale yellow prisms, m. p. 116° (Found : Cl + Br, 41·3. Calc.: 41·2%), giving a bright red *sodium* salt. The *phenylhydrazone* crystallised from alcohol in small, orange needles, m. p. 241° (decomp.) (Found : Cl + Br, 31·3%). The mixed m. p.'s with the isomerides above were depressed. Orange-red colours were given by aqueous and alcoholic alkalis.

Nitration of 2-Chloro-3-bromo-4-hydroxybenzaldehyde.—This process was carried out with quantities as for 4-chloro-3-bromo-2-hydroxybenzaldehyde, but at 30—40° for one hour. *2-Chloro-3-bromo-5-nitro-4-hydroxybenzaldehyde* crystallised from glacial acetic acid in long, golden-yellow, silky needles, m. p. 140° (Found : Cl + Br, 40·9%). Bromination as above of the mononitration product of 2-chloro-4-hydroxybenzaldehyde gave an identical product, m. p. and mixed m. p. 140°. The identical *phenylhydrazones* crystallised from alcohol in very deep purple plates, m. p. 205° (decomp.) (Found : Cl + Br, 30·9, 31·0. Calc.: 31·2%), and gave brownish-red colours with aqueous and alcoholic alkalis.

Nitration of 4-Bromo-2-hydroxybenzaldehyde.—(*a*) *Mononitration.*

The aldehyde (3 g.) was nitrated as for the 2-chloro-4-hydroxy-compound, 6 g. of nitric acid being used. The product, *4-bromo-5-nitro-2-hydroxybenzaldehyde*, was entirely volatile in steam and crystallised from alcohol in very pale yellow rosettes, m. p. 128° (Found: Br, 32·3. $C_7H_4O_4NBr$ requires Br, 32·5%), which were slightly soluble in cold, but readily soluble in hot water and in the usual solvents. The *phenylhydrazone* crystallised from alcohol in small, orange needles, m. p. 189° (Found: Br, 23·6. $C_{13}H_{10}O_3N_3Br$ requires Br, 23·8%), its yellow solution being deepened by alkalis. The p-*nitrophenylhydrazone*, yellow micro-needles, m. p. 301° (decomp.) (Found: Br, 21·2. $C_{13}H_9O_5N_4Br$ requires Br, 21·0%), gave a cherry-red colour with alkalis, turning bluer on dilution. The *semicarbazone*, pale yellow micro-needles, decomposed above 210° (Found: Br, 26·2. $C_8H_7O_4N_4Br$ requires Br, 26·4%).

(*b*) *Dinitration*. The aldehyde (2 g.), dissolved in glacial acetic acid (5 c.c.), was nitrated at 0° with fuming nitric acid (3 c.c.), and heated at 100° for 10 minutes; *4-bromo-3:5-dinitro-2-hydroxybenzaldehyde* was separated from volatile products by steam-distillation and then crystallised from alcohol in colourless plates and from dilute acetic acid in colourless needles, m. p. 143° (Found: Br, 27·3. $C_7H_3O_6N_2Br$ requires Br, 27·5%). The *phenylhydrazone* crystallised from alcohol in small orange needles, m. p. 209° (decomp.) (Found: Br, 20·8. $C_{13}H_9O_5N_4Br$ requires Br, 21·0%), and its yellow solution was turned brown by caustic alkalis. The p-*nitrophenylhydrazone*, light orange micro-needles, m. p. 250° (decomp.) (Found: Br, 18·6. $C_{13}H_8O_7N_5Br$ requires Br, 18·77%), gave a deep red colour in concentrated solution with caustic alkalis, which became bluer on dilution. The *semicarbazone*, light yellow micro-needles, had m. p. 224° (decomp.) (Found: Br, 22·7. $C_8H_6O_6N_5Br$ requires Br, 23·0%).

Nitration of 2-Bromo-4-hydroxybenzaldehyde.—(*a*) *Mononitration*. Quantities and procedure as for the previous isomeride. *2-Bromo-5-nitro-4-hydroxybenzaldehyde* was much more slowly volatile in steam than the chloro-analogue and also more soluble in water; it crystallised from alcohol in pale yellow needles, m. p. 131° (Found: Br, 32·7. $C_7H_4O_4NBr$ requires Br, 32·5%), gave an orange-red *silver* salt and a bright green *copper* salt. The *phenylhydrazone*, fine, silky, purple needles, had m. p. 181° (decomp.) (Found: Br, 23·5. $C_{13}H_{10}O_3N_3Br$ requires Br, 23·8%), and gave a reddish-brown colour with aqueous alkalis. The p-*nitrophenylhydrazone*, orange micro-needles, m. p. 265° (decomp.) (Found: Br, 20·8%), gave violet-red colours with alkalis, turning bluer on dilution. The *semicarbazone*, light orange micro-needles, had m. p. 267° (decomp.) (Found: Br, 26·1%).

(*b*) *Dinitration*. The aldehyde (2 g.), dissolved in glacial acetic acid

(15 c.c.), was nitrated with 63% nitric acid (3 g.) in the cold and then kept at 50° for 3 hours; *2-bromo-3 : 5-dinitro-4-hydroxybenzaldehyde* was non-volatile in steam and crystallised from water in massive pale yellow prisms, m. p. 110° (Found: Br, 27·4%), slightly soluble in water; it gave a deep golden-brown colour with ferric chloride, but did not reduce ammoniacal silver nitrate or Fehling's solution. The brown, flocculent *silver* salt was soluble in water. The *phenylhydrazone* crystallised from alcohol in dark purple plates, m. p. 186° (decomp.) (Found : Br, 20·8%), the golden-brown solution being changed to reddish-brown by caustic alkalis. The p-*nitrophenylhydrazone*, brown micro-needles, m. p. 248° (decomp.) (Found : Br, 18·9%), gave violet-red colours with caustic alkalis, turning bluer on dilution. The *semicarbazone*, orange micro-needles, had m. p. 188° (decomp.) (Found : Br, 22·9%).

Nitration of 2 : 3-dibromo-4-hydroxybenzaldehyde gave *2 : 3-dibromo-5-nitro-4-hydroxybenzaldehyde*, m. p. 155° (Found : Br, 49·0. $C_7H_3O_4NBr_2$ requires Br, 49·2%), identical with the brominated product from the mono-nitrated 2-bromo-4-hydroxybenzaldehyde, m. p. and mixed m. p. 155°, the procedures being as for the chloro-analogues. Their identical *phenylhydrazones* crystallised from alcohol in deep purple parallelepipeds, m. p. 204° (decomp.) (Found : Br, 38·3, 38·6. $C_{13}H_9O_3N_3Br_2$ requires Br, 38·5%), and gave brownish-red colours with aqueous and alcoholic alkalis.

Nitration of 3 : 4-dibromo-2-hydroxybenzaldehyde gave *3 : 4-dibromo-5-nitro-2-hydroxybenzaldehyde*, which crystallised from alcohol in pale yellow needles, m. p. 114° (Found : Br, 48·8%), and did not depress the m. p. of the product obtained by the bromination of the mononitrated 4-bromo-2-hydroxybenzaldehyde (above).

4 : 5-Dibromo-2-hydroxybenzaldehyde, colourless needles, m. p. 132° (Found : Br, 57·2%), was prepared in the same way as 4-chloro-5-bromo-2-hydroxybenzaldehyde (*loc. cit.*). It gives a yellow *silver* salt. The p-*nitrophenylhydrazone* crystallised from glacial acetic acid in deep orange-brown micro-needles, m. p. 266° (decomp.) (Found : Br, 38·4%), and gave deep bluish-red colours with alkalis. *4 : 5-Dibromo-3-nitro-2-hydroxybenzaldehyde* crystallised from alcohol in pale yellow prisms, m. p. 118° (Found : Br, 49·1%). The *silver* salt is deep orange. The *phenylhydrazone* crystallised from alcohol in orange needles, m. p. 236° (decomp.) (Found : Br, 38·4%), and gave a deep red colour with aqueous caustic alkalis.

Nitration of 4-Iodo-2-hydroxybenzaldehyde.—(*a*) *Mononitration.* The aldehyde (2 g.), dissolved in glacial acetic acid (6 c.c.), was treated with fuming nitric acid (3 g.), kept for 2½ hours, and then heated at 45° for 5 minutes; the mixture was diluted with water, nearly neutralised by alkali, and steam-distilled.

4-*Iodo-5-nitro-2-hydroxybenzaldehyde* (1·5 g.), which passed over, crystallised from alcohol in small golden-yellow needles, m. p. 118° (Found : I, 42·9. $C_7H_4O_4NI$ requires I, 43·3%). The yellow *silver* salt was only sparingly soluble in water. The *phenylhydrazone*, small, old-gold needles, had m. p. 177° (decomp.) (Found : I, 33·0. $C_{13}H_{10}O_3N_3I$ requires I, 33·2%) and gave a brown colour with alkalis. The p-*nitrophenylhydrazone*, bright yellow micro-needles, m. p. 297° (decomp.) (Found : I, 29·3. $C_{13}H_9O_5N_4I$ requires I, 29·7%), gave violet-red colours with alkalis, turning bluer on dilution. The *semicarbazone*, pale yellow micro-needles, decomposed at 230—240° (Found : I, 35·9. $C_8H_7O_4N_4I$ requires I, 36·2%).

3-*Bromo-4-iodo-5-nitro-2-hydroxybenzaldehyde* crystallised from alcohol in small pale yellow needles, m. p. 145° (Found : Br + I, 55·9. $C_7H_3O_4NBrI$ requires Br + I, 55·6%).

(*b*) *Dinitration*. In the above process the residue (0·5 g.) after steam-distillation was 4-*iodo-3 : 5-dinitro-2-hydroxybenzaldehyde*, which crystallised from alcohol in small, brown needles, m. p. 160° (Found : I, 37·8. $C_7H_3O_6N_2I$ requires I, 37·6%). The *silver* salt was light orange. The *phenylhydrazone*, small, light brown needles, had m. p. 229° (decomp.) (Found : I, 30·0. $C_{13}H_9O_5N_4I$ requires I, 29·7%) and gave brown colours with alkalis. The p-*nitrophenylhydrazone*, brownish-orange micro-needles, m. p. 257° (decomp.) (Found : I, 26·4. $C_{13}H_8O_7N_5I$ requires I, 26·8%), gave deep violet-red colours with alkalis. The *semicarbazone*, light brownish-yellow micro-needles, decomposed when heated (Found : I, 31·8. $C_8H_6O_6N_5I$ requires I, 32·15%).

5-*Bromo-4-iodo-2-hydroxybenzaldehyde* is slowly volatile in steam and crystallises from alcohol in very pale yellow needles, m. p. 117° (0·1100 g. gave 0·1428 g. AgX. Calc. : 0·1422 g.), and its rather insoluble *sodium* salt in golden spangles. It gives a yellow *silver* salt. The *phenylhydrazone* crystallises in slender, pale yellow needles, m. p. 151°, and the p-*nitrophenylhydrazone* in orange micro-needles, m. p. 266° (decomp.), which give deep bluish-red colours with aqueous alkalis.

5-*Bromo-4-iodo-3-nitro-2-hydroxybenzaldehyde* crystallises from alcohol in small, golden-yellow prisms, m. p. 153° (0·1042 g. gave 0·1180 g. AgX. Calc. : 0·1185 g.), and gives an orange *silver* salt. The *phenylhydrazone* crystallises from alcohol in deep orange needles, m. p. 245° (decomp.) (0·1000 g. gave 0·0922 g. AgX. Calc. : 0·0915 g.), and gives a deep red colour with aqueous caustic alkalis.

Nitration of 2-Iodo-4-hydroxybenzaldehyde.—(*a*) *Mononitration*. A method giving better results than the foregoing was to nitrate the aldehyde (4·5 g.), dissolved in acetic anhydride (12 c.c.), with diacetylorthonitric acid (4 c.c.) added in two portions, the temperature

not being allowed to exceed 40—50°. After being kept for 15 minutes at 50°, the mixture was diluted and steam-distilled; *2-iodo-5-nitro-4-hydroxybenzaldehyde*, which passed over, crystallised from alcohol in small, colourless prisms, m. p. 162° (Found : I, 43·5. $C_7H_4O_4NI$ requires I, 43·3%). The orange *silver* salt was sparingly soluble in water. The *phenylhydrazone*, very dark purple needles, had m. p. 204° (decomp.) (Found : I, 33·3%) and gave golden-brown solutions with alcoholic alkalis. The p-*nitrophenylhydrazone*, reddish-brown micro-needles, m. p. 273° (Found : I, 29·8%), gave violet-red colours with alkalis. The *semicarbazone*, light brown micro-needles, had m. p. 211° (decomp.) (Found : I, 36·6%).

3-Bromo-2-iodo-5-nitro-4-hydroxybenzaldehyde crystallises from dilute acetic acid in pale yellow needles, m. p. 178° (Found : Br + I, 55·8%). An authentic specimen had m. p. 178°.

(*b*) *Dinitration*. Procedure as for the analogues. *2-Iodo-3 : 5-dinitro-4-hydroxybenzaldehyde* crystallised in massive yellow prisms, m. p. 162° (Found : I, 37·5%). The colours of the *silver* and *copper* salts were canary-yellow and bright green, respectively. The *phenylhydrazone*, deep brownish-purple needles, had m. p. 197° (decomp.) (Found : I, 30·0%), and gave a reddish-brown solution with alkalis. The p-*nitrophenylhydrazone*, dark-red micro-needles, m. p. 240° (decomp.) (Found : I, 27·2%), gave a reddish-violet colour with aqueous sodium hydroxide, which changed to reddish-pink on heating. The *semicarbazone*, orange micro-needles, had m. p. 205° (decomp.) (Found : I, 32·4%).

3-Bromo-2-iodo-4-hydroxybenzaldehyde crystallises from alcohol in pale yellow prisms, m. p. 204° (Found : AgX, 129·7. $C_7H_4O_2BrI$ requires AgX, 129·4%).

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CCXCVII.—*The Quadrivalency of Selenium. Part I. 4-Carboxydiphenyl and* p-*Carboxyphenyl Methyl Selenoxides.*

By WILSON ROBINSON GAYTHWAITE, JOSEPH KENYON, and HENRY PHILLIPS.

THE resolution of 4′-amino-4-methyldiphenyl sulphoxide (I) and *m*-carboxyphenyl methyl sulphoxide (II) into their optically active forms (Harrison, Kenyon, and Phillips, J., 1926, 2079) provided

conclusive experimental evidence that the double bond between sulphur and oxygen in these compounds is unsymmetrical and can

$$\text{(I.)}\quad {NH_2\cdot C_6H_4 \atop Me\cdot C_6H_4}{>}\overset{+}{S}-\overset{-}{O} \qquad\qquad {HO_2C\cdot C_6H_4 \atop Me}{>}\overset{+}{S}-\overset{-}{O}\quad \text{(II.)}$$

therefore be considered to be a semipolar double bond. In order to obtain evidence as to the nature of the bonds linking the selenium and oxygen atoms of selenoxides, attempts have now been made to resolve *phenyl* p-*tolyl selenoxide* (III), *4-carboxydiphenyl selenoxide* (IV), and p-*carboxyphenyl methyl selenoxide* (V), but they

$$ {Me\cdot C_6H_4 \atop Ph}{>}SeO \qquad {HO_2C\cdot C_6H_4 \atop Ph}{>}SeO \qquad {HO_2C\cdot C_6H_4 \atop Me}{>}SeO $$

(III.) (IV.) (V.)

have been unsuccessful. This failure was unexpected since the sulphoxides were resolved without difficulty, and the resolution of *dl*-phenylmethylselenetine *d*-bromocamphorsulphonate by Pope and Neville (J., 1902, **81**, 1552) proves that quadrivalent selenium has a tetrahedral environment.

The chemical evidence at our disposal suggests that the linking between the selenium and oxygen atoms may be partly polar in character. For example, the selenoxides now described, to a greater degree even than the sulphoxides of similar constitution, are much more soluble in acids than in water.

The selenoxides, however, differ from sulphoxides in one important respect. Sulphoxides are so readily oxidised with potassium permanganate to the corresponding sulphones that it is often difficult, even when mild oxidising reagents are nsed, to arrest the oxidation of a sulphide at the sulphoxide stage. It is noteworthy, therefore, that the selenoxides described could not be oxidised to selenones hy potassium permanganate, and also that with the exception of diphenyl selenone (Krafft and Vorster, *Ber.*, 1893, **26**, 2820), which has the properties of a peroxide and hence differs considerably from its inert sulphur analogue, no reference to the isolation of selenones can be found in the literature. This particular reluctance on the part of a selenium atom, linked to two univalent groups and to oxygen, to pass to the sexavalent condition is also illustrated by the crystallisation of benzeneseleninic acid as a nitrate from moderately concentrated nitric acid (which would oxidise benzenesulphinic acid to the sulphonic acid); moreover, although the interaction of ethyl iodide and silver sulphite leads to the formation of the unsymmetrical ethyl ethanesulphonate, yet silver selenite, under the same conditions, yields the symmetrical diethyl selenite (Michaelis and Landmann, *Annalen*, 1887, **241**, 150).

It can therefore be concluded that the linking between the

selenium and oxygen atoms of a selenoxide may be partly polar in character, but at the same time may tend to utilise or render inert the remaining combining capacity of the selenium atom in a manner which suggests that the linking may not be an unsymmetrical semipolar double bond. The partly polar character of the linking might be accounted for by assuming that the oxygen atom is linked to the selenium atom by two semipolar single bonds (Prideaux, *Chem. and Ind.*, 1923, **42**, 672; Sugden, J., 1927, 1173); until the electronic structure of such bonds is precisely defined, however, it is difficult to visualise why two such bonds, when exerted together towards the same atom, should differ from a semipolar double bond, and further, why, by exerting two semipolar single bonds, the selenium atom should lose combining capacity.

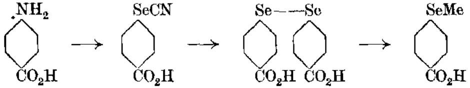
These difficulties could be overcome by assuming that two selenium electrons and one oxygen electron are concerned with the formation of each semipolar single bond, but that only one of the electrons—a selenium electron—is shared by both atoms, the remaining selenium electron and oxygen electron of the trio being assumed to be in some way essential for the formation of a semipolar single bond and no longer available for purposes of reaction. By the aid of these assumptions it would be possible to explain, not only the reluctance on the part of the selenium atom to become sexavalent, but also the possible symmetrical disposition of the oxygen atom in space with respect to the remainder of the selenoxide molecule. To determine whether this hypothesis is valid other selenoxides are being prepared and investigated.

Phenyl *p*-tolyl selenoxide was prepared by the action of alkalis on phenyl *p*-tolyl selenide dibromide. On cooling warm solutions of this selenoxide in aqueous solutions of *d*-camphorsulphonic acid, indefinite mixtures of the two separated, and the selenoxide recovered from the mother-liquors was optically inactive; but when equimolecular proportions were mixed in warm, dry ethyl acetate crystals were deposited which, by titration, were found to agree closely in composition with that demanded for the *d*-camphorsulphonate of the selenoxide. The rotatory powers of these " salts " in dry ethyl acetate were, however, identical with the rotatory powers of the solutions obtained by dissolving *d*-camphorsulphonic acid and the selenoxide in ethyl acetate in the same proportions as they occurred in the " salts."

4-Carboxydiphenyl selenoxide was prepared by the oxidation of phenyl *p*-tolyl selenide with an excess of potassium permanganate, and was not contaminated by the corresponding selenone. It gave well-defined, crystalline salts with brucine, *l*-menthylamine, and *d*-α-phenylethylamine, the properties of the salts being un-

changed by repeated crystallisation from various solvents. The selenoxide regenerated from the salts was, in every instance, optically inactive. Although, when free, 4-carboxydiphenyl selenoxide does not form a dihydroxide, its salt with *d*-α-phenylethylamine was carefully examined after it had been in contact with water or wet solvents, in order to make certain that the failure to obtain resolution was not due to the addition of water to the possibly unsymmetrical selenoxide, giving rise to a symmetrical dihydroxide. No evidence for such combination could be obtained, and no change in the rotatory power of a dry specimen of this salt could be produced by recrystallising it from dry ethyl acetate.

p-Carboxyphenyl methyl selenoxide was prepared from the dibromide of the corresponding selenide, which was synthesised according to the following scheme. It gave a brucine salt which furnished no evidence that it was a mixture of stereoisomerides.



E X P E R I M E N T A L.

Phenyl p-*tolyl selenide* was obtained by the method used by Krafft and Vorster (*loc. cit.*) for the preparation of diphenyl selenide. Phenyl *p*-tolyl sulphone (116 g.), which has m. p. 127—128° and not 124·5° as quoted in the literature, and powdered selenium (40 g.) were heated in a metal-bath until there was an active evolution of sulphur dioxide : after 2—3 hours the temperature was raised, and phenyl *p*-tolyl selenide distilled at 305—312°. By redistillation it was obtained as an almost odourless, pale yellow, mobile liquid, b. p. 175—178°/20 mm.; yield 35 g. (Found : C, 63·2; H, 4·9. $C_{13}H_{12}Se$ requires C, 63·1 ; H, 4·8%). The *dibromide* was prepared hy the addition of bromine (6·5 g.) to a cooled solution of the selenide (10 g.) in carbon disulphide (20 c.c.). After standing for an hour, the crystalline material (14 g., m. p. 143—144°) was removed by filtration and recrystallised from carbon disulphide whereby it was obtained as long, orange-red, glistening needles, m. p. 149—150° (Found : Br, 39·2. $C_{13}H_{12}SeBr_2$ requires Br, 39·4%).

Phenyl p-*tolyl selenoxide* was readily obtained by trituration of the dibromide (7·5 g.) with sodium hydroxide solution (15 c.c. of 15%) until the reddish-brown paste became converted into a white, granular powder; this was filtered off, washed, dried, and crystallised from benzene, from which it separated in clusters of feathery needles,

m. p. 131—133°; yield 4 g. The selenoxide was also prepared directly from the selenide by the action of a boiling solution of potassium permanganate. When the theoretical amount of potassium permanganate was used the yield of selenoxide was only about 25% because further oxidation of a portion of the material to 4-carboxydiphenyl selenoxide took place and therefore a considerable proportion of the selenide was recovered unchanged. *Phenyl p-tolyl selenoxide* prepared in this way had m. p. 131—133° either alone or when mixed with that prepared from the dibromide (Found: C, 59·7; H, 4·5. $C_{13}H_{12}OSe$ requires C, 59·3; H, 4·5%). The selenoxide, when triturated with saturated aqueous hydrobromic acid, was rapidly transformed into the orange-red dibromide, which after crystallisation from carbon disulphide had m. p. 149—150° (decomp.) either alone or when mixed with the dibromide prepared directly from the selenide.

Attempted Resolution of Phenyl p-*Tolyl Selenoxide by Means of* d-*Camphorsulphonic Acid.*—Phenyl *p*-tolyl selenoxide (1·3 g.) was added to a solution of *d*-camphorsulphonic acid (3 g.) in water (5 c.c.), and the mixture heated on the steam-bath for a few minutes until solution was almost complete. After cooling, the crystalline material was filtered off and found to consist of almost pure selenoxide which was optically inactive. The recovered selenoxide was therefore dissolved in a solution of *d*-camphorsulphonic acid (2 g.) in ethyl alcohol (12 c.c.), and the solution allowed to crystallise. After decomposition of the filtrate with sodium carbonate, 0·18 g. of selenoxide was obtained which proved to be optically inactive.

The selenoxide (2·6 g.) and *d*-camphorsulphonic acid (2·3 g.) were dissolved in hot, dry ethyl acetate. The crystals which separated on cooling the resulting clear solution had α_{5461} + 0·32° in dry ethyl acetate (c = 1·1175; l = 2·0), whence $[\alpha]_{5461}$ + 14·3°. By titration, 0·2235 g. of the crystals was found to contain 0·0908 g. of *d*-camphorsulphonic acid, whereas if the crystals had been the pure salt of the selenoxide they should have contained 0·1045 g. of the acid. A solution prepared by making up 0·1327 g. of the selenoxide and 0·0908 g. of *d*-camphorsulphonic acid to 20 c.c. with dry ethyl acetate had α_{5461} + 0·33° (l = 2·0) whence $[\alpha]_{5461}$ + 14·7°. Hence it was concluded that no resolution of the selenoxide was taking place. The filtrate from the crystals described above deposited on standing a second crop which had α_{5461} + 0·30° in dry ethyl acetate (c = 1·0725; l = 2·0) whence $[\alpha]_{5461}$ + 13·9°. This second crop contained slightly more than the theoretical quantity of *d*-camphorsulphonic acid, since 0·2847 g. contained 0·1409 g. of acid (theory requires 0·1331 g.).

4-*Carboxydiphenyl selenoxide* was prepared by boiling an aqueous

suspension of phenyl *p*-tolyl selenide and potassium permanganate for several hours. The manganese mud was dissolved and the 4-carboxydiphenyl selenoxide precipitated by the passage of sulphur dioxide. The reaction mixture was filtered and the insoluble portion macerated with dilute sodium carbonate solution. In this way, the products of the oxidation were separated into phenyl *p*-tolyl selenoxide and 4-carboxydiphenyl selenoxide. On the addition of dilute sulphuric acid to the sodium carbonate extract, 4-carboxydiphenyl selenoxide separated and was obtained, after crystallisation from alcohol, as a microcrystalline powder, m. p. 253—255° (decomp.) (Found : C, 53·5; H, 3·4; equiv., by titration, 292. $C_{13}H_{10}O_3Se$ requires C, 53·2; H, 3·4%; equiv., 293).

4-*Carboxydiphenyl selenide* was prepared by warming a mixture of 4-carboxydiphenyl selenoxide (0·5 g.), acetic acid (15 c.c.), and zinc dust (0·3 g.) on a steam-bath for 3 hours. The hot filtered solution was diluted with water and the selenide (0·25 g.) separated as pale yellow, glistening leaflets, m. p. 182—184° (without decomp.) (Found : equiv., by titration, 279. $C_{13}H_{10}O_2Se$ requires equiv., 277).

4-*Carboxydiphenyl selenide dibromide* was prepared (*a*) by the addition of aqueous hydrobromic acid to a warm solution of 4-carboxydiphenyl selenoxide (0·5 g.) in acetic acid, from which it separated as yellow, microcrystalline needles (0·6 g.), which turn deep red and soften between 180—190° and melt at 208—210°; (*b*) by the addition of a solution of bromine (0·13 g.) in carbon tetrachloride (1 c.c.) to a warm solution of 4-carboxydiphenyl selenide (0·21 g.) in the same solvent (50 c.c.). The dibromide (0·28 g.), m. p. 205—207°, crystallised on cooling the mixed solutions (0·1534 g. neutralised 0·0560 g. KOH on decomposition. Calc.: 0·0588 g.).

Attempted Resolution of 4-Carboxydiphenyl Selenoxide.—The *brucine* salt of 4-carboxydiphenyl selenoxide was prepared in warm acetone solution, from which it separated on cooling as very small needles, m. p. 130° (decomp.). The *strychnine* salt was too unstable to be of service. The l-*menthylamine* salt crystallised from alcohol in needles, m. p. 220—222° (decomp.). Its rotatory power, $[\alpha]_{5461} - 16{\cdot}4°$ ($c = 0{\cdot}8415$ in ethyl alcohol; $l = 2{\cdot}0$), and m. p. remained unchanged after repeated crystallisation from alcohol. The d-α-*phenylethylamine* salt was prepared in aqueous solution, from which it separated in clusters of feathery needles, m. p. 194—195° (decomp.). Recrystallisation from alcohol, water, or ethyl acetate caused no change in either its m. p. or its rotatory power, which was $[\alpha]_{5461} - 12{\cdot}7°$ ($c = 1{\cdot}139$ in pyridine; $l = 2{\cdot}0$). This salt was also heated at 98°/15 mm., but such treatment did not cause it to lose weight or to change in rotatory power.

4 : 4′-*Dicarboxydiphenyl diselenide* was prepared by the method used by Bauer (*Ber.*, 1913, **46**, 92) for the preparation of analogous compounds. To a vigorously stirred, cooled solution of *p*-amino-benzoic acid (46 g.) in water (750 c.c.) and concentrated hydrochloric acid (83 c.c.), sodium nitrite solution (230 c.c. of 10%) was added. After 30 minutes, the solution was made alkaline to Congo-red by the addition of potassium acetate, and a solution of potassium selenocyanate (96 c.c. of 50%) was then gradually added. After the mixture had been stirred for 3 hours, the light brown, insoluble material was removed by filtration; it consisted mainly of an inseparable mixture of *p*-carboxyphenyl selenocyanate contaminated with 4 : 4′-dicarboxydiphenyl diselenide. In order to convert the selenocyanate into the diselenide, the mixture was dissolved in 2*N*-sodium hydroxide solution, and the solution boiled for an hour, cooled, filtered and acidified. The precipitated 4 : 4′-dicarboxy-diphenyl diselenide (32 g.) separated from methyl alcohol as a pale yellow, microcrystalline powder, m. p. 297° (Found: C, 42·1; H, 2·5. $C_{14}H_{10}O_4Se_2$ requires C, 42·0; H, 2·5%).

p-*Carboxyphenyl methyl selenide.* To a gently boiling solution of 4 : 4′-dicarboxydiphenyl diselenide (40 g.) in aqueous sodium hydroxide (240 c.c. of 10%), sodium hydrosulphite (80 g.) (or zinc dust, 12 g.) was gradually added. To the filtered and cooled solution, methyl sulphate (13 c.c.) was added in small portions with agitation, and after 1 hour the crude p-*carboxyphenyl methyl selenide* was precipitated by the addition of acid. When dry, it was extracted with benzene, in which the chief impurity, the diselenide, is insoluble; 20 g. separated from hot benzene as a pale yellow, microcrystalline powder, m. p. 174° (Found: C, 44·8; H, 3·8. $C_8H_8O_2Se$ requires C, 44·6; H, 3·7%). The *dibromide* was prepared by the addition of a solution of bromine (9·6 g.) in acetic acid (50 c.c.) to a slightly warm solution of the selenide (12·80 g.) in acetic acid (200 c.c.). The addition compound (22·4 g.) rapidly separated as small orange-red needles, which, after washing with acetic acid, turned a deep red above 170° and had m. p. 198—199° (Found: Br, 42·3. $C_8H_8O_2SeBr_2$ requires Br, 42·7%).

p-*Carboxyphenyl methyl selenoxide* was obtained (*a*) by triturating the dibromide (22·4 g.) with water (60 c.c.) and a few c.c. of 3*N*-sodium hydroxide solution until the suspension had turned completely white, the liquor being acid to Congo-red, removing the selenoxide (9·80 g.) by filtration, washing with water and drying, m. p. 170° (indef.); (*b*) by the addition of hydrogen peroxide (5 c.c. of 30%) to a solution of *p*-carboxyphenyl methyl selenide (10·2 g.) in methyl alcohol (300 c.c.), and filtering the crystals (10 g.) of *p*-carboxyphenyl methyl selenoxide which separated over-night.

It crystallised from alcohol in small, hard, irregular prisms, m. p. 183—184° (decomp.) (Found: C, 41·2; H, 3·7. $C_8H_8O_3Se$ requires C, 41·6; H, 3·5%), and the molten product rapidly set to a yellow solid which remelted about 250°.

The *brucine* salt of *p*-carboxyphenyl methyl selenoxide had m. p. 105—110° (see below); it was very soluble in cold alcohol, and when recrystallised from a hot mixture of alcohol and acetone was obtained with m. p. 151—153°. On investigation, it was found that during the recrystallisation the selenoxide had become partly reduced to the selenide and that the alkaloidal salt (m. p. 151—153°) was a mixture of the brucine salts of the selenoxide and the selenide. Accordingly the brucine salt was prepared in cold absolute ethyl alcohol and the solution allowed to concentrate in a desiccator until a suitable amount (m. p. 105—110°, decomp.) had separated. From this salt the selenoxide (m. p. 183—184°, decomp.) could be obtained by decomposition with alkalis and acidification of the alkaline extract with acetic acid. Similarly, by the addition of dilute sodium carbonate solution to the filtrate from the brucine salt, aqueous solutions of the sodium salt of *p*-carboxyphenyl methyl selenoxide were prepared. These solutions after repeated extraction with chloroform to remove dissolved brucine were found to be either optically inactive or in some cases to give a rotation of the order α_{5461} + 0·02°—0·04°, *i.e.*, within the limits of experimental error. The various solutions of the sodium salt yielded *p*-carboxyphenyl methyl selenoxide (as shown by its m. p., and by conversion into the dibromide by means of hydrobromic acid) which was optically inactive in either aqueous or ethyl-alcoholic solution. The brucine salt of *p*-carboxyphenyl methyl selenoxide is optically inactive to light of λ_{5461} and has $[\alpha]_{5870}$ + 2·5° (l = 2·0; c = 0·9864 in ethyl alcohol).

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CCXCVIII.—*The Quadrivalency of Selenium. Part II. The Simple Halogen Derivatives and the Dihydroxide of 4-Acetamidodiphenyl Selenide.*

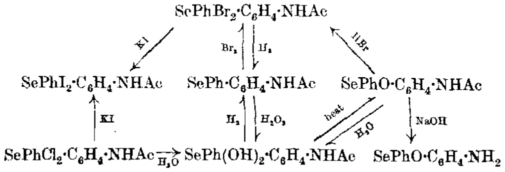
By WILSON ROBINSON GAYTHWAITE, JOSEPH KENYON, and HENRY PHILLIPS.

THE primary object of this investigation was to prepare and attempt the resolution of *4-aminodiphenyl selenoxide*. This selenoxide can be prepared indirectly from *4-aminodiphenyl selenide*, which is formed by the interaction of benzeneseleninic acid with aniline,

but it proved to be unstable in the presence of acids and hence its resolution could not be attempted. 4-*Acetamidodiphenyl selenide*, however, reacts with halogens in acetic acid solution to give well-defined, highly coloured, crystalline dihalogen derivatives, the chemical properties of which have been studied in order to compare and contrast them with those of the dihalogen derivatives of semi-aromatic and aliphatic selenides. When heated, the *dichloride* and also the *dibromide* are converted into selenides with halogenated aromatic nuclei. The corresponding *di-iodide*, however, under the same treatment evolves iodine and, indeed, even when exposed to the air at the ordinary temperature, gradually reverts to the selenide.

An aqueous solution of potassium bromide converts the dichloride into the dibromide, and this with an aqueous solution of 2 mols. of potassium iodide yields the di-iodide. Each of the three dihalogen compounds can be recrystallised from glacial acetic acid, but only the di-iodide is sufficiently soluble in ethyl alcohol to be recrystallised from this solvent. When the di-iodide is treated with a suitable amount of dry ether, a less highly coloured substance remains undissolved, which proves to be the selenide. Similarly, the selenide is deposited when an ethereal solution of the di-iodide is concentrated. The di-iodide in ethereal solution therefore dissociates into iodine and the selenide.

Water, or more rapidly dilute alkalis, converts the dichloride and dibromide into the *dihydroxide*. Boiling water, however, is without action on the di-iodide which with sodium hydroxide yields its parent selenide. By the action of moist silver oxide, the di-iodide can be made to yield the dihydroxide, which is nevertheless contaminated with some selenide, the latter being the sole product when the di-iodide is treated with warm aqueous solutions of either potassium iodide or sodium thiosulphate. These reactions can be summarised as follows :



4-Acetamidodiphenyl selenide dihydroxide can also be obtained by the action of hydrogen peroxide on the selenide, and can be recrystallised from hot water. On fusion (147—148°) it loses water,

and the corresponding selenoxide is formed, which, when heated more strongly, darkens, suddenly evolves oxygen, and leaves a fluid mass of pure 4-acetamidodiphenyl selenide. This behaviour is in marked contrast to that of 4-amino-4′-methyldiphenyl sulphoxide which can be heated well above its m. p. without showing any sign of decomposition. At a lower temperature and pressure, 4-acetamidodiphenyl selenide dihydroxide loses water in a manner which is strongly reminiscent of the conversion of α-dimethyltelluronium dihydroxide into a telluroxide (Vernon, J., 1920, **117**, 86, 889). By the action of the halogen acids on aqueous solutions of this telluroxide, Vernon obtained *dimethyltelluronium dihalides*, which differed in chemical and physical properties from the corresponding dihalogen compounds obtained from aqueous solutions of the β-dimethyltelluronium dihydroxide; he concluded that the four groups of the isomeric dimethyltelluronium dihydroxides were in the same plane as the central tellurium atom, and that the α-base was the *trans*-isomeride, whilst the telluroxide after recombination with water gave the *cis*-isomeride.

$$\underset{\alpha\text{-}trans.}{\begin{matrix}CH_3\\HO\end{matrix}\!>\!Te\!<\!\begin{matrix}OH\\CH_3\end{matrix}} \xrightarrow{-H_2O} \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!Te{=}O \xrightarrow{+H_2O} \underset{\beta\text{-}cis.}{\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!Te\!<\!\begin{matrix}OH\\OH\end{matrix}}$$

No analogous change occurs, however, when 4-acetamidodiphenyl selenide dihydroxide loses water, since the same dihalogen compounds were obtained from the dihydroxide as from the selenoxide. These dihalogen compounds were also identical with those prepared from 4-acetamidodiphenyl selenide by the direct addition of halogen.

The behaviour of the dihalogen derivatives and dihydroxide of 4-acetamidodiphenyl selenide is therefore consistent with a constitution such as $\begin{matrix}NHAc{\cdot}C_6H_4\\C_6H_5\end{matrix}\!>\!\overset{+}{Se}\!<\!\begin{matrix}X\\\bar{X}\end{matrix}$.

It may be pointed out, however, that during all the reactions described, the selenide molecule remains intact and in no instance is a carbon–selenium bond broken. The ease with which 4-acetamidodiphenyl selenoxide loses oxygen is noteworthy as suggesting, but in no way proving, that oxygen may be linked to selenium by a linking weaker than a semipolar double bond.

EXPERIMENTAL.

4-*Aminodiphenyl selenide* was prepared by heating a mixture of benzeneseleninic acid (20 g.) and aniline (80 c.c.) at 110—115° for 6 hours. After removal of the unchanged aniline in a current of steam, the dark-coloured residue was extracted with hot dilute hydrochloric acid. On addition of sodium carbonate to the acid

extract, the selenide was precipitated as a pink, microcrystalline powder (yield, 12—15 g.). 4-Aminodiphenyl selenide separates *from aqueous alcohol (norit) in clusters of almost colourless, prismatic* needles, m. p. 93—94° (Found : N, 5·7. $C_{12}H_{11}NSe$ requires N, 5·6%). The base is readily soluble in hot dilute hydrochloric acid, and on cooling, the ***hydrochloride*** separates as small, feathery needles, m. p. 159° (Found: HCl, by titration, 13·0. $C_{12}H_{12}NSeCl$ requires HCl, 12·9%). Addition of sodium carbonate solution to the hydrochloride regenerates the pure base.

By the interaction of aniline and benzenesulphinic acid, Hinsberg (*Ber.*, 1908, **41**, 113) obtained 4-aminodiphenyl sulphoxide. The foregoing reaction of benzeneseleninic acid doubtless proceeds by the same mechanism, but the selenoxide produced is reduced to the selenide by the excess of aniline.

4-*Acetamidodiphenyl selenide* was prepared by warming together 4-aminodiphenyl selenide (3·8 g). and acetic anhydride (4 c.c.). The product (4·2 g.) separated from aqueous alcohol in glistening leaflets, m. p. 169—170° (Found: C, 58·2; H, 5·0; N, 4·8. $C_{14}H_{13}ONSe$ requires C, 57·9: H, 4·4; N, 4·8%). 4-Acetamidodiphenyl selenide decomposes when heated with mineral acids. It undergoes hydrolysis smoothly, however, under the following conditions : A solution of the selenide (2 g.) in alcohol (10 c.c.) was heated under reflux with 3*N*-sodium hydroxide solution (10 c.c.) for 6 hours; on cooling, the regenerated base (1·65 g.) crystallised from the reaction mixture, and after crystallisation from alcohol, had m. p. 93—94°.

4-*Acetamidodiphenyl Selenide Dihydroxide*.—To a cooled mixture of 4-acetamidodiphenyl selenide (5·8 g.) and glacial acetic acid (10 c.c.), perhydrol (4 c.c.) was gradually added; the *dihydroxide* (5·7 g.) separated from the resulting clear solution on standing, and after crystallisation from boiling water (700 c.c.) had m. p. 147—148° (decomp.) (*Found : C, 51·9; H, 5·0; N, 4·3.* $C_{14}H_{15}O_3NSe$ requires C, 51·9; H, 4·6; N, 4·3%). When a large excess of perhydrol was used the same compound was obtained, and no trace of the corresponding selenone could be detected. When heated for a few minutes with zinc dust and glacial acetic acid 4-acetamidodiphenyl selenide dihydroxide was quantitatively reduced to the corresponding selenide. It dissolved in warm *N*/2-hydrochloric acid, and when the solution was heated on the steam-bath for an hour glistening leaflets of 4-acetamidodiphenyl selenide separated. Some of the dissolved dihydroxide reappeared as tarry material and the solution possessed oxidising properties, consistent with the view that it contained hypochlorous acid which had resulted from the dissociation of a selenide hydroxychloride. 4-Acetamidodiphenyl

selenide dihydroxide was melted over a small flame and the colourless liquid heated until there was no further loss of moisture (Found : H_2O, 5·56. Calc. : 5·55%). When the horny mass thus obtained was heated more strongly, it darkened, suddenly evolved a gas, and the residual fluid became crystalline on cooling. By recrystallisation from alcohol, this residue was obtained as colourless leaflets (1·0 g.), m. p. 166—168°, either alone or when mixed with 4-acetamidodiphenyl selenide.

4-Acetamidodiphenyl Selenoxide.—4-Acetamidodiphenyl selenide dihydroxide (4 g.) when heated under a pressure of 20 mm. effervesced vigorously at 120—130° and became fluid. After 20 minutes, the effervescence ceased and the liquid crystallised although its temperature was 130°. The solid, *4-acetamidodiphenyl selenoxide*, was recrystallised from dry chloroform and obtained as small, ill-defined crystals, m. p. 144—146° (Found: C, 54·8; H, 4·6; N, 4·6. $C_{14}H_{13}O_2NSe$ requires C, 54·9; H, 4·3; N, 4·6%). Unlike the original dihydroxy-compound, the selenoxide does not decompose on melting: the m. p. of the dihydroxy-compound is really the temperature at which it loses water at ordinary pressure.

When a hot aqueous-alcoholic solution of 4-acetamidodiphenyl selenoxide was cooled, crystals of the corresponding dihydroxide, m. p. 147—148° (decomp.), were deposited. The dihalides, obtained in quantitative yields by the addition of concentrated solutions of hydrochloric, hydrobromic, or hydriodic acid to a warm solution of the selenoxide in glacial acetic acid, were identical with the dihalides obtained in a similar manner from the corresponding dihydroxide.

4-Aminodiphenyl selenoxide was prepared by heating a solution of 4-acetamidodiphenyl selenide dihydroxide (1·7 g.) in alcohol (15 c.c.) with sodium hydroxide solution (10 c.c. of 3*N*) for 6 hours; on cooling, the selenoxide (1·3 g.) separated as glistening needles, m. p. 188—189° (decomp.) (Found: C, 54·4; H, 4·1; N, 5·4; Se, 30·4. $C_{12}H_{11}ONSe$ requires C, 54·6; H, 4·2; N, 5·3; Se, 30·0%). This compound was also prepared from 4-aminodiphenyl selenide as follows: The selenide (7·5 g.), dissolved in acetone (30 c.c.), was mixed with perhydrol (4·5 c.c.), and the crystals (5·2 g.) which separated on standing were filtered off and washed with acetone (m. p. 180—181°). They were recrystallised, together with a second crop (0·6 g.) obtained from the filtrate, from methyl alcohol, and then had m. p. 187—189° either alone or when mixed with the selenoxide prepared from 4-acetamidodiphenyl selenide dihydroxide as described above. 4-Aminodiphenyl selenoxide was quantitatively reduced to the corresponding selenide by treatment with zinc dust and a solution of sodium hydroxide.

Reaction with dilute hydrochloric acid. The finely-powdered

selenoxide (1 g.) was triturated with dilute hydrochloric acid (50 c.c. of *N*/2). The reaction mixture was filtered, and from the acid filtrate *4-aminodiphenyl selenide* (0·2 g.), m. p. 93—94°, was precipitated by the addition of sodium bicarbonate. No crystalline product could be isolated from the tarry, insoluble material.

4-Acetamidodiphenyl selenide dichloride was prepared by the addition of a mixture of concentrated aqueous hydrochloric acid (2 c.c.) and acetic acid (3 c.c.) to a warm solution of the dihydroxide (1·53 g.) in glacial acetic acid (4 c.c.); the dichloride which separated crystallised from acetic acid (30 c.c.) as almost colourless, bulky, feathery needles (1·6 g.), which turned yellow about 125° and had m. p. 131—132° (Found: Cl, 19·6. $C_{14}H_{13}ONCl_2Se$ requires Cl, 19·6%). When chlorine was passed into a solution of 4-acetamidodiphenyl selenide in acetic acid, a white, crystalline compound was precipitated, m. p. 186—187°, which contained chlorine not displaceable by the action of aqueous sodium hydroxide. Even when the equivalent amount of chlorine, dissolved in acetic acid, was added to an acetic acid solution of the selenide, the product obtained melted indefinitely at 110—120°. Thus chlorine, in contradistinction to bromine and iodine, appears to react with the acetamido-group. By treatment either with much water or with dilute sodium hydroxide solution, the dichloride was converted quantitatively into the dihydroxide, whilst when triturated with a cold, concentrated, aqueous solution of potassium bromide (2 mols.), it was rapidly and quantitatively converted into the brightly coloured dibromide.

4-Acetamidodiphenyl selenide dibromide was prepared by mixing solutions of bromine (1·8 g.) and 4-acetamidodiphenyl selenide (3·5 g.) in acetic acid (95 c.c. in all); hemispherical clusters of small red needles (5·05 g.) separated rapidly. After recrystallisation from warm glacial acetic acid, the dibromide turned bright red at 100° and melted to a deep red liquid at 135—136° (Found: C, 37·2; H, 3·9; N, 3·1; Br, 35·1. $C_{14}H_{13}ONBr_2Se$ requires C, 37·3; H, 2·9; N, 3·1; Br, 35·4%). When zinc dust was added to a suspension of the dibromide in acetic acid, 4-acetamidodiphenyl selenide was obtained. On grinding with sodium hydroxide solution (35 c.c. of 3*N*), the highly coloured dibromide (17·6 g.) was converted into the colourless dihydroxide (10 g.), m. p. 147—148°, with evolution of steam. The same reaction was effected, only more slowly, by the use of cold water. Hydrobromic acid was evolved when 4-acetamidodiphenyl selenide dibromide was heated at its m. p. for ½ hour; the resulting deep red paste was washed with ether, and the insoluble grey powder was crystallised from alcohol, from which it separates as colourless, glistening needles, m. p. 167°.

This *compound* contains bromine but gives no precipitate when heated with alcoholic silver nitrate solution (Found: Br, 34·7. $C_{14}H_{11}ONBr_2Se$ requires Br, 35·2%); the bromine had therefore migrated from the selenium atom to one of the benzene nuclei, producing, probably, 3 : 5-dibromo-4-acetamidodiphenyl selenide.

4-*Acetamidodiphenyl selenide di-iodide.* (*a*) A solution of iodine (1·3 g.) in warm acetic acid (29 c.c.) was added to a solution of 4-acetamidodiphenyl selenide (1·45 g.) in acetic acid (30 c.c.); after a few minutes, the *di-iodide* separated in bulky rosettes of fine needles (2·3 g.), m. p. 144—145° (decomp.) (Found: I, by titration, 46·6. $C_{14}H_{13}ONI_2Se$ requires I, 46·7%). (*b*) Concentrated aqueous hydriodic acid (10 c.c.) was added to a warm solution of the di-hydroxide (0·8 g.) in acetic acid (10 c.c.), and the di-iodide (1·0 g.), m. p. 144—145° (decomp.) either alone or when mixed with the compound prepared as described under (*a*) or (*c*), was obtained. Furthermore, when 4-acetamidodiphenyl selenoxide was used in the above experiment in place of the dihydroxide, an identical di-iodide was obtained. (*c*) The dibromide (1·12 g.) was triturated with a solution of potassium iodide (0·83 g.; 2 mols.) in water (1 c.c.) during 20 minutes; the orange dibromide gradually changed to the chocolate-brown di-iodide, which was washed with water and recrystallised from alcohol or acetic acid.

4-Acetamidodiphenyl selenide di-iodide, when heated at its m. p. for an hour, gave a copious sublimate of iodine, whilst the residue, after crystallisation from aqueous alcohol, had m. p. 93—94° either alone or when mixed with 4-acetamidodiphenyl selenide. This change proceeds slowly at ordinary temperatures: a specimen of the di-iodide exposed to the air was found to have changed completely to the selenide after 10 days.

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CCXCIX.—*The Quadrivalency of Selenium. Part III. The Instability of the Compounds of Quadrivalent Selenium derived from Phenyl Methyl and Phenyl Ethyl Selenides and Phenyl- and* p-*Tolyl-selenoglycollic Acids.*

By OWEN KEMPSTER EDWARDS, WILSON ROBINSON GAYTHWAITE, JOSEPH KENYON, and HENRY PHILLIPS.

OWING to their instability, much difficulty has been experienced in the preparation of selenoxides containing an alkyl group attached to the selenium atom. Such selenoxides have been found to decom-

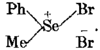
pose on heating mainly as indicated by the equation $SeRO{\cdot}CH_2R = SeRH + O{:}CHR$. They differ widely in this respect from purely aromatic selenoxides, such as 4-acetamidodiphenyl selenoxide, which, as described in the preceding communication, decomposes on heating into the corresponding selenide and oxygen.

Sulphoxides containing an alkyl group attached to the sulphur atom are known to undergo a similar change. For example, Fromm and Achert (*Ber.*, 1903, **36**, 534) obtained benzaldehyde by heating benzyl sulphoxide; Smythe (*J.*, 1909, **95**, 349) showed that during the interaction of this sulphoxide with hydrogen chloride in various solvents, benzaldehyde, benzyl mercaptan, dibenzyl disulphide, and benzyl chloride were produced. Similarly, Fichter and Sjöstedt (*Ber.*, 1910, **43**, 3422) and Fichter and Wenk (*Ber.*, 1912, **45**, 1373) showed that the controlled electrochemical oxidation of phenyl ethyl sulphide yielded phenyl mercaptan and acetaldehyde. Pummerer (*Ber.*, 1909, **42**, 2282; 1910, **43**, 1404), who investigated the conversion of phenyl- and *p*-tolyl-sulphoxyacetic acids into glyoxylic acid and the corresponding aromatic thiols (by the agency of heat or traces of mineral acids), was led to suggest, as the underlying cause, the tendency on the part of such sulphoxides to assume an isomeric form by a process analogous to the keto-enol change. On the electronic conceptions of valency, Pummerer's formulation of the initial step in the decomposition could be written

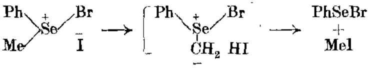
$$R{\cdot}\overset{+}{\underset{\underset{-}{O}}{S}}{\cdot}CH_2R \longrightarrow R{\cdot}\overset{+}{\underset{OH}{S}}{\cdot}\overset{-}{C}HR\,.$$

Since we find that selenoxides of analogous constitution to the sulphoxides mentioned decompose in a similar fashion, it is possible that selenoxides also may undergo an isomeric change of this nature. The following compounds of quadrivalent selenium have therefore been investigated in order to obtain evidence as to whether the migration of hydrogen is an initial phase of their decomposition.

Phenyl methyl selenide dibromide, prepared by the addition of bromide to phenyl methyl selenide, is a well-defined, bright red crystalline substance. On heating at about 100° it decomposed quantitatively into methyl bromide and bromoselenobenzene. When triturated at 40° with a concentrated solution of potassium iodide, the dibromide was converted into the *di-iodide*; if, however, the dibromide was treated with a cold solution of potassium iodide of the same concentration, a *bromo-iodide* was obtained in theoretical yield. This compound, on heating, decomposed quantitatively to give methyl iodide and bromoselenobenzene. These results clearly

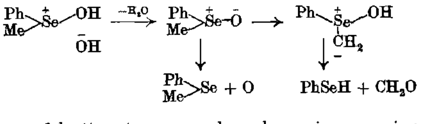
indicate that the bromine atoms of phenyl methyl selenide dibromide are *not linked in the same manner to the selenium atom*, and hence agree with a formula such as  .

The facility with which the dibromide and the bromo-iodide decompose into alkyl halogen compounds and bromoselenobenzene is most marked, and that the presence of the methyl group is in some way responsible is evident, since diphenyl selenide dibromide (Krafft and Lyons, *Ber.*, 1894, **27**, 1761) has been found to decompose into bromodiphenyl selenide and hydrobromic acid, whilst 4-acetamidodiphenyl selenide dibromide yields 3 : 5-(?)dibromo-4-acetamidodiphenyl selenide and hydrobromic acid (preceding communication). The mode of decomposition of phenyl methyl selenide bromo-iodide is therefore not inconsistent with the view that such decompositions pass through a preliminary phase, as indicated below, which involves the loss of a proton by the methyl group and causes this group to become less firmly attached to the selenium atom.



Phenyl ethyl selenide dibromide was also found to decompose quantitatively when heated at 130° into ethyl bromide and bromoselenobenzene.

Phenyl methyl selenide dihydroxide, prepared by treating a solution of the dibromide in water with silver oxide, and concentrating the filtrate in a vacuum, was obtained as a viscous oil, which, when heated at 100°/15 mm. or at 170°/760 mm., decomposed yielding phenyl methyl selenide, diphenyl diselenide, and formaldehyde. The phenyl methyl selenide may have been produced by the reduction of the dihydroxide or selenoxide by the other products of the decomposition. The formation of formaldehyde is in agreement with the view that phenyl methyl selenoxide may exist in two isomeric forms which, being unstable, decompose thus:



Unsuccessful attempts were made under various experimental

conditions to cause phenyl methyl selenide dihydroxide to lose water and yield a selenoxide. These experiments led to the conclusion that the selenoxide, when formed, immediately decomposed, and they were therefore abandoned.

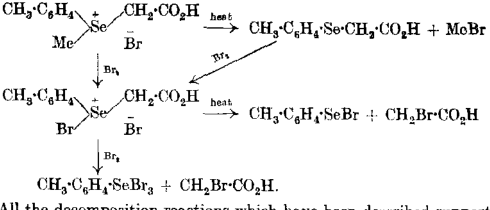
Phenyl ethyl selenide dihydroxide, prepared from the dibromide by similar methods, was found to be less stable than its lower homologue, and decomposed yielding mainly diphenyl diselenide, even when left in a vacuum desiccator containing sulphuric acid.

Phenyl- and p-*Tolyl-methylselenetine Bromides*.—Phenylmethylselenetine bromide, prepared by the method of Pope and Neville (J., 1902, **81**, 1552), was found to decompose smoothly and quantitatively at its m. p. into methyl bromide and phenylselenoglycollic acid :

$$\frac{Ph}{Me}\!>\!\overset{+}{Se}\!<\!\frac{CH_2{\cdot}CO_2H}{\bar{B}r} \longrightarrow CH_2(SePh){\cdot}CO_2H + MeBr$$

Similarly, *phenylselenoglycollic acid dibromide* decomposed when heated, yielding bromoselenobenzene and bromoacetic acid. Attempts were made to prepare phenylethylselenetine bromide by the interaction of phenyl ethyl selenide and bromoacetic acid: phenylselenoglycollic acid was, however, the only product isolated, owing, presumably, to the ease with which the selenetine bromide produced decomposed.

p-*Tolylmethylselenetine bromide* was also prepared from *p*-tolyl methyl selenide and bromoacetic acid. On heating, it softened at 85—88°, turned more definitely crystalline, and finally became molten at 96—97°, the m. p. of *p*-tolylselenoglycollic acid (Morgan and Porritt, J., 1925, **127**, 1758). When treated with a molecular proportion of bromine in cold carbon tetrachloride solution, *p*-tolylmethylselenetine bromide was converted into *p*-tolylselenoglycollic *acid dibromide* which, on heating, decomposed smoothly into *p*-bromoselenotoluene and bromoacetic acid. The replacement of the methyl group of *p*-tolylmethylselenetine bromide by means of bromine occurs with great readiness. This possibly explains why we were unable to obtain *p*-tolylselenoglycollic acid tetrabromide by the action of excess of bromine on *p*-tolylselenoglycollic acid, as described by Morgan and Porritt (*loc. cit.*). We found, in agreement with the results of our other experiments, that the dibromide produced as an initial stage of the reaction was converted by the excess of bromine into *p*-bromoselenotoluene dibromide and bromoacetic acid. The results of the experiments with these compounds can be summarised as follows :



All the decomposition reactions which have been described support the contention that the withdrawal of aliphatic groups from their combination with quadrivalent selenium may be facilitated by their ability to provide a proton. The most striking example is the decomposition of *p*-tolylselenoglycollic acid dibromide, which does not decompose into *p*-tolylselenoglycollic acid and bromine, as might be expected (compare Morgan and Porritt, *loc. cit.*), but into bromoselenotoluene and bromoacetic acid.

EXPERIMENTAL.

The Action of Heat on Phenylmethylselenetine Bromide.—Phenylmethylselenetine bromide was prepared by the method of Pope and Neville (*loc. cit.*). Equimolecular amounts of phenyl methyl selenide (8·6 g.) and bromoacetic acid (7·0 g.) were gently warmed until molten and allowed to stand over-night; dry ether was then added to the reaction mixture from which a mass of crystals had separated. The white, additive compound (7·6 g.) removed by filtration had m. p. 110—111°, with evolution of a gas. After recrystallisation from a mixture of alcohol and ether, the phenylmethylselenetine bromide had m. p. 111° as recorded by Pope and Neville.

0·4665 G. of this bromide was heated at about 110° until the evolution of gas had ceased; the gas was passed into an aqueous-alcoholic solution of silver nitrate and produced a copious precipitate of silver bromide. The residual product when cold weighed 0·3256 g., the loss being 30·2% (Calc. for loss of CH_3Br, 30·6%). The residual product was an acid (Found: equiv., 230. Phenylselenoglycollic acid, $C_6H_5{\cdot}Se{\cdot}CH_2{\cdot}CO_2H$, requires equiv., 215). The acid thus obtained in another experiment was seeded with phenylselenoglycollic acid and set to a mass of colourless crystals, m. p. 36—37°, either alone or when mixed with phenylselenoglycollic acid prepared by the method of Morgan and Porritt (*loc. cit.*). (Although the acid was obtained as described by these authors, yet the physical constants recorded by them, b. p. 160°/750 mm., m. p.

40°, are considerably different from those now found, *viz.*, b. p. 197—198°/10 mm., m. p. 36—37°.)

It was not found possible to synthesise phenylmethylselenetine bromide from phenylselenoglycollic acid and methyl bromide. A dry ethereal solution of these two substances was kept in a stoppered bottle for 50 days, but did not deposit crystals of the insoluble selenetine bromide. Further, phenylmethylselenetine bromide was heated in a sealed tube at 110° until completely molten; after 24 hours, the tube (the contents of which were still fluid) was opened and found to be under considerable pressure, which was due to the presence of methyl bromide, since the still molten contents of the tube crystallised when inoculated with a crystal of phenylselenoglycollic acid.

Phenylselenoglycollic acid dibromide was prepared by the addition of a solution of bromine (8 g.) in warm carbon tetrachloride (50 c.c.) to a hot solution of phenylselenoglycollic acid (10·75 g.) in carbon tetrachloride (500 c.c.). The additive compound (18·3 g.; yield 97%) separated in very small, yellow, ill-defined needles, which melted at 126° to a deep red liquid (Found : Br, 42·3. $C_8H_8O_2Br_2Se$ requires Br, 42·7%), and were almost insoluble in carbon tetrachloride, chloroform, benzene, or carbon disulphide; they dissolved in about 10 times their weight of hot glacial acetic acid, but on cooling, the solution deposited deep red crystals of bromoselenobenzene, m. p. 61°, in almost theoretical amount (Found : Br, 33·9. Calc. : Br, 33·9%).

Action of Heat on Phenylselenoglycollic Acid Dibromide.—(*a*) When this dibromide (3·7 g.) was heated, the products of decomposition distilled at 100—102°/12 mm. and set to a brownish-red, crystalline mass. When about two-thirds of the material had distilled, the temperature began to rise and the distillation was stopped. The distillate was separated by light petroleum into brownish-red crystals of bromoselenobenzene (m. p. 61°) and very hygroscopic, colourless plates, m. p. 46° (see below). The undistilled residue was separated by means of warm light petroleum into bromoselenobenzene and diphenyl diselenide (m. p. 63°). (*b*) Phenylselenoglycollic acid dibromide (3·7 g.) was melted and the cooled melt extracted several times with cold light petroleum; the residue consisted of almost colourless crystals which separated from hot light petroleum in transparent, colourless leaflets, m. p. 46—47°, either alone or when mixed with bromoacetic acid. The extracts on evaporation gave bromoselenobenzene together with a small amount of diphenyl diselenide. It is therefore evident that phenylselenoglycollic acid dibromide decomposes at its m. p. mainly thus : $CH_2(SeBr_2Ph)\cdot CO_2H = PhSeBr + CH_2Br\cdot CO_2H$.

p-*Tolylmethylselenetine Bromide.*—A cold liquid mixture of *p*-tolylmethyl selenide (3·7 g.) and bromoacetic acid (2·8 g.), after standing over-night, set to a mass of long, glistening needles, which, when separated from the admixed oil by means of porous earthenware, weighed 3·7 g. A portion (0·2 g.) of this *p*-tolylmethylselenetine bromide was placed in a test tube and plunged into boiling water; the compound slowly melted, without visible effervescence, but a strong odour of methyl bromide was developed. The resulting oil immediately set to a crystalline mass, m. p. 96—97°, either alone or when mixed with *p*-tolylselenoglycollic acid (Morgan and Porritt, *loc. cit.*). 0·1964 G., heated until completely molten, lost 0·0582 g. (Found: loss, 29·7. Calc. for CH_3Br, 29·3%).

p-Tolylselenoglycollic acid dibromide (compare Morgan and Porritt, *loc. cit.*) was prepared by two methods. (*a*) A solution of bromine (1·4 g.) in carbon tetrachloride (25 c.c.) was added to a hot solution of *p*-tolylselenoglycollic acid (1·8 g.) in the same solvent (100 c.c.); the yellow needles of the additive compound (3·1 g.) melted at 103—104° to a deep red liquid. (*b*) A solution of bromine (0·4 g.) in carbon totrachloride (25 c.c.) was added to a cold solution of *p*-tolylmethylselenetine bromide (0·65 g.) in carbon tetrachloride (300 c.c.); the yellow needles (0·8 g.), which began to separate immediately, had m. p. 100—101°, either alone or when mixed with the dibromide prepared as in (*a*).

Action of heat on p-*tolylselenoglycollic acid dibromide.* This compound (1·5 g.) was heated at its m. p. for a few minutes, and the deep red liquid, which set to a semicrystalline mass on cooling, was extracted several times with small amounts of cold light petroleum; the insoluble residue (0·43 g.) consisted of colourless, hygroscopic leaflets, m. p. 48—49° either alone or when mixed with bromoacetic acid. The extracts, on evaporation at the ordinary temperature, gave a reddish-brown oil which could not be induced to crystallise; that it is *p*-bromoselenotoluene is rendered highly probable by its ready reduction with aluminium amalgam in moist ethereal solution to di-*p*-tolyl diselenide, m. p. 47°; aluminium bromide was obtained on washing the ethereal solution with water.

p-*Bromoselenotoluene dibromide* was prepared by three methods. (*a*) *p*-Tolueneseleninic acid (1·02 g.) was triturated with concentrated aqueous hydrobromic acid (6 c.c.), and the orange-red powder (2 g., m. p. 80—90°) which separated was recrystallised from chloroform; red needles, m. p. 113—114° (decomp.). (*b*) A solution of bromine (0·5 g., 3 mols.) in carbon tetrachloride (15 c.c.) was added to a warm solution of di-*p*-tolyl diselenide (0·34 g.) in warm carbon tetrachloride (25 c.c.); on cooling, orange-red leaflets

(0·6 g.) separated, m. p. 114—115° (decomp.). (c) Solutions of bromine (0·9 g., 2 mols.) and of *p*-tolylselenoglycollic acid (0·57 g.) in chloroform (20 c.c. in all) were mixed and became warm; on cooling, deep red needles were deposited, m. p. 113—114° (decomp.) either alone or when mixed with the compound prepared as described under (*a*) or (*b*). There can be no doubt therefore that this compound is actually *p*-bromoselenotoluene dibromide, and not *p*-tolylselenoglycollic acid tetrabromide as supposed by Morgan and Porritt (*loc. cit.*). *p*-Bromoselenotoluene dibromide dissolves in hot water and the resulting colourless solution on cooling deposits colourless needles, m. p. 169—170° either alone or when mixed with *p*-tolylseleninic acid.

If preparation (*c*) be attempted in carbon tetrachloride, of which 100 c.c. are necessary to dissolve the acid, the sole product of the reaction is *p*-tolylselenoglycollic acid dibromide.

Phenyl methyl selenide dibromide was prepared by the addition of bromine (33 g.) in carbon disulphide (30 c.c.) to phenyl methyl selenide (35 g.) in the same solvent (120 c.c.). The warm solution deposited the additive compound almost immediately as long, yellow, glistening needles (yield 95%) which turned brown at about 100° and melted at 115—116° (decomp.); it is soluble in water to the extent of about 6%, and the colourless solution is acid to Congo-red and when cooled or concentrated deposits the dibromide unchanged in m. p. (Found: Br, 48·0. $C_7H_8SeBr_2$ requires Br, 48·3%).

Action of heat on phenyl methyl selenide dibromide. The dibromide (1·9940 g.) was heated at 120—130° for about 10 minutes, by which time decomposition had ceased. The evolved gas was passed into an alcoholic solution of silver nitrate and caused the precipitation of silver bromide. The loss in weight was 0·5684 g. or 28·50% (Calc. for loss of CH_3Br, 28·46%). The non-volatile residue set to a brownish-red, crystalline mass, m. p. 60—61°, which separated from light petroleum as deep garnet-red cubes, m. p. 61°, alone or when mixed with bromoselenobenzene.

Phenyl methyl selenide di-iodide was prepared by triturating the dibromide (2 g.) at 40° with a solution of potassium iodide (2 g.; 2 mols.) in water (10 c.c.). The chocolate-coloured powder obtained (2·65 g.; calc., 2·60 g.), after washing and drying had m. p. 67—70°, and crystallised from alcohol in glistening, purple, short prisms, m. p. 69—71° (Found: I, 59·4. $C_7H_8I_2Se$ requires I, 59·8%).

Phenyl methyl selenide bromo-iodide was prepared by triturating phenyl methyl selenide dibromide (3 g.) with a cold solution of potassium iodide (3 g.; 2 mols.) in water (15 c.c.). The bromo-iodide (3·5 g.), was deep red and separated from alcohol in red,

ill-defined, compact crystals (3·1 g.), m. p. 85° (decomp.) (Found: Br + I, 55·5. C_7H_8BrISe requires Br + I, 54·8%). When triturated with a warm solution of potassium iodide it was immediately converted into the di-iodide, m. p. and mixed m. p. 67—70° (decomp.).

The action of heat on phenyl methyl selenide bromo-iodide. 1·0056 G. of the bromo-iodide were heated at 100° and the distillate was collected. The non-volatile residue weighed 0·7636 g. (Found: loss, 34·1. Calc., for MeI, 37·5%; for MeBr, 25·1%), and when crystallised from light petroleum had m. p. 61°, either alone or mixed with bromoselenobenzene. The distillate was a colourless liquid which was non-volatile at the ordinary temperature, contained iodine, and combined with pyridine on warming. Phenyl methyl selenide bromo-iodide therefore decomposes on heating according to the equation SePhMeBrI = SePhBr + MeI.

Phenyl methyl selenide dihydroxide was prepared by the trituration of a mixtnre of phenyl methyl selenide dibromide (10 g.), silver oxide (12 g.), and water (100 c.c.) until the yellow colour of the dibromide had disappeared. The colourless filtered solution on evaporation and desiccation gave about 8 c.c. of a viscous oil which could not be induced to crystallise. This compound was not analysed since it could not be completely freed from moisture without decomposition, but its identity was established by its immediate conversion into phenyl methyl selenide dibromide, m. p. 115—116°, on the addition of aqueous hydrobromic acid.

Action of heat on phenyl methyl selenide dihydroxide. The above compound (4 c.c.), contained in a small distilling flask, was gradually heated in an oil-bath; at 135—155° (bath temp.) some of the admixed water distilled, and at 175—180° one or two drops of an oily material distilled over and dissolved in the water into which the side-arm of the flask dipped; at 185°, a sudden decomposition ensued and some material distilled. The residue in the flask (about 1 g.) set immediately to a yellow, crystalline mass, m. p. 63—64°, after inoculation with a crystal of diphenyl diselenide. The water into which the products of decomposition had been led contained globules of oil, which was isolated with ether and distilled; the distillate (about 1 g.) had b. p. 202—203° and was identified as phenyl methyl selenide by its complete conversion into the dibromide, m. p. 115—116°. The water, after removal of the oil, gave a silver mirror with ammoniacal silver oxide, restored the colour to Schiff's reagent, gave the characteristic odour of formalin on evaporation, and left a small amount of white, amorphous, insoluble material. There can thus be little doubt that formaldehyde is one of the decomposition products of phenyl methyl selenide dihydroxide. Similar

products were obtained when the decomposition was carried out at 100°/15 mm.

Phenyl ethyl selenide dibromide was prepared by mixing phenyl ethyl selenide (5·55 g.) and a solution of bromine (4·9 g.) in carbon disulphide (20 c.c.). After several hours, the separated crystalline material (10 g.), m. p. 79°, was crystallised from ether and obtained as light red, transparent, stout, prismatic rods melting at 84° to a deep red liquid (Found : Br, 46·4. $C_8H_{10}Br_2Se$ requires Br, 46·4%).

Action of heat on phenyl ethyl selenide dibromide. This compound (2·0044 g.) was heated in a bath at a temperature not exceeding 130° until decomposition was complete (10 mins.). The residue (1·3738 g.) set to a brownish-red, crystalline mass, m. p. 60—61°. The vapour evolved during the decomposition gave a copious precipitate of silver bromide when passed into an aqueous-alcoholic solution of silver nitrate. The decomposition of the dibromide therefore takes place according to the equation $SePhEtBr_2 = SePhBr + EtBr$ (Found : loss, 31·3. Calc. for loss of C_2H_5Br, 31·6%). The solid product of the decomposition separated from light petroleum as deed garnet-red cubes, m. p. 61° either alone or when mixed with bromoselenobenzene.

Interaction of Phenyl Ethyl Selenide and Bromoacetic Acid.—Phenyl ethyl selenide (5·55 g.) and bromoacetic acid (4·17 g.) were mixed and a little dry ether was added to render the mixture homogeneous. After standing for 3 weeks, the product had set to a mass of crystals, which, after draining on porous earthenware, had m. p. 35—36° either alone or when mixed with phenylselenoglycollic acid of m. p. 36—37°.

Action of Heat on Diphenyl Selenide Dibromide.—Diphenyl selenide and diphenyl diselenide were prepared by the method of Krafft and Lyons (*Ber.*, 1894, **27**, 1761). Diphenyl selenide dibromide was obtained in 95% yield by mixing bromine (4·9 g.) and diphenyl selenide (7 g.) each dissolved in 15 c.c. of carbon disulphide. This solvent is preferable to ether, since the m. p. of the diphenyl selenide dibromide (154°, unaltered by recrystallisation) obtained by its use is 14° higher than that recorded by Krafft and Lyons (*loc. cit.*). When heated, diphenyl selenide dibromide (5·0 g.) melted to a deep red liquid which effervesced vigorously owing to the evolution of hydrogen bromide. After 10 minutes, the evolution of gas ceased and the loss in weight was 20% (Calc. for 1HBr, 20·6%). The residue, a semi-solid mixture, was separated by means of light petroleum into an oil and an almost colourless, crystalline solid, which crystallised from hot light petroleum as glistening leaflets (0·5 g.), m. p. 115·5°. This compound is evidently dibromodiphenyl selenide, isolated by Krafft and Lyons (*loc. cit.*). The oil distilled completely at 196—198°/12 mm. to give an almost

colourless liquid which deposited glassy crystals (2·0 g.), m. p. 32—33° (Found: Br, 25·6. $C_{12}H_9BrSe$ requires Br, 25·6%). Since this *compound* was the principal product of the thermal decomposition of diphenyl selenide dibromide, it follows that the main course of the reaction can be represented by the equation $SePh_2Br_2 = Ph{\cdot}Se{\cdot}C_6H_4Br + HBr$, and that the equation given by Krafft and Lyons, *viz.*, $2SePh_2Br_2 = Ph_2Se + (C_6H_4Br)_2Se + 2HBr$, represents a side reaction. These results explain why the attempt made by these authors to isolate diphenyl diselenide from the products of decomposition was unsuccessful.

Diphenyl selenoxide, prepared by the action of sodium hydroxide solution on diphenyl selenide dibromide, after recrystallisation from benzene had m. p. 113—114° (Krafft and Lyons, *loc. cit.*). This compound is more conveniently prepared by the following method: To diphenyl selenide (7 g.), perhydrol (10 c.c.) was added in small portions. The reaction mixture set, on cooling, to a crystalline mass; cold water was added and the product filtered, but as the selenoxide obtained weighed only 6·45 g. (instead of the calculated 7·5 g.), the aqueous filtrate (50 c.c.) was mixed with hydrobromic acid until no further reddish-yellow crystalline precipitate was formed. The latter, filtered and dried (1·75 g.), had m. p. 152—153° either alone or when mixed with diphenyl selenide dibromide. This result shows that diphenyl selenoxide is soluble in cold water to the extent of 2·2%. Diphenyl selenoxide, after crystallisation from benzene, has m. p. 113—114°, either alone or when mixed with the selenoxide prepared by the action of sodium hydroxide on diphenyl selenide dibromide.

The authors desire to express their indebtedness to the Government Grant Committee of the Royal Society for a grant which has helped to defray the cost of these investigations. One of them (W. R. G.) wishes to thank the Department of Scientific and Industrial Research for a maintenance grant which has enabled him to participate in this work.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, June 18th*, 1928.]

CCC.—*The Use of Toluenesulphonic Esters in Place of Halogen Esters in Malonic Ester Syntheses.*

By DAVID HENRY PEACOCK and PO THA.

ALTHOUGH the esters of *p*-toluenesulphonic acid are readily prepared and have found many applications in syntheses, there appears to be no record of their use in conjunction with sodiomalonic ester;

moreover, since such esters are sometimes more readily accessible *than the halogen esters, the reaction appeared worthy of examination.* As was to be expected, it took place much more slowly than when the halogen esters are used, but the experiments show that the toluenesulphonates are equally suitable, in spite of a similar tendency to form dialkylmalonic esters from equimolecular proportions of sodiomalonic and toluenesulphonic esters.

The results may prove especially useful in the preparation of substances containing the phenoxyethyl or phenoxypropyl groups, for these derivatives are of value in a number of syntheses. Thus, phenoxyethylmalonic acid is usually prepared from a phenoxyethyl halide (see, *e.g.*, Bently, Haworth, and Perkin, J., 1896, **69**, 169), but the corresponding alcohol is much more readily prepared than the bromide (Kirner, *J. Amer. Chem. Soc.*, 1926, **48**, 2749), and one of us has found that it is readily converted into *β-phenoxyethyl* p-*toluenesulphonate*, an easily purified crystalline substance which reacts smoothly with sodiomalonic ester to give phenoxyethylmalonic ester. The derivatives of phenoxyethylmalonic acid are thus readily accessible by this route.

Experimental.

(1) Ethyl malonate (16 g.), methyl *p*-toluenesulphonate (18·6 g.), sodium (2·3 g.), and absolute alcohol (78 c.c.) were boiled under reflux until the reaction was complete (4 hrs.). The product was worked up in the usual way and 13·9 g. of ester, b. p. 105—110°/30 mm., were obtained; this was converted by the action of strong ammonia into the amide which, after crystallisation from alcohol, had m. p. 209°. Since the m. p. of malonamide is 170°, and that of methylmalonamide is variously given as 206—212°, it is clear that the alkylation had been successful.

(2) Ethyl malonate (80 g.), ethyl *p*-toluenesulphonate (100 g.), sodium (11·5 g.), and absolute alcohol (300 c.c.) were boiled under reflux for 20 hours, and the product was worked up in the usual way, 63 g. (yield 68%) of the ester being obtained; hydrolysis with alcoholic potash gave ethylmalonic acid, m. p. 111—112° (Conrad, *Annalen*, 1880, **204**, 136, gives m. p. 111·8°, and malonic acid has m. p. 132°). The silver salt of the butyric acid prepared from this ethylmalonic acid in the usual way was analysed (Found: Ag, 55·1. Calc.: Ag, 55·3%).

(3) Phenoxyethylmalonic acid was prepared as follows. Phenoxyethyl alcohol was obtained by boiling a mixture of phenol (188 g.), caustic soda (80 g.), ethylene chlorohydrin (120 g.), and water (720 c.c.) under reflux for ½ hour. The product was worked up in the usual way and the yield was 163 g. (79%). This alcohol can be

converted into its *p*-toluenesulphonate by heating with the acid chloride at 110—120°, but this is better prepared as follows (compare Foldi, *Ber.*, 1920, **53**, 1836): To 70 g. of phenoxyethyl alcohol, 100 g. of *p*-toluenesulphonyl chloride and 100 c.c. of caustic soda solution (containing 20 g. NaOH) are added with shaking during ½ hour. At first the mixture is cooled under the tap, but it becomes almost solid when the ester begins to separate and the temperature is therefore allowed to rise. The mixture is finally heated for ½ hour on a steam-bath to complete the reaction. *β-Phenoxyethyl* p-*toluenesulphonate* separates as an oil which solidifies on being poured into cold water (crude yield, 90%). When crystallised from methylated spirit, it separates in stout prisms, m. p. 80° (Found: C, 61·4; H, 5·4. $C_{15}H_{16}O_4S$ requires C, 61·6; H, 5·5%). The reactions of this ester with ammonia, amines, and *p*-toluenesulphonamide have been examined by one of us and will be communicated later. Ethyl phenoxyethylmalonate was prepared by heating together 1·15 g. of sodium, 8 g. of ethyl malonate, 15 g. of β-phenoxyethyl *p*-toluenesulphonate, and 25 c.c. of absolute alcohol under reflux for 20 hours. On being worked up in the usual way the mixture gave phenoxyethylmalonic acid, which, when crystallised from toluene, had m. p. 134—136° (compare Bently, Haworth, and Perkin, *loc. cit.*) (Found: C, 58·7; H, 5·3. Calc.: C, 58·9; H, 5·35%).

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CCCI.—*Dibenzyl Ether as a Cryoscopic Solvent.*

By GEORGE MACDONALD BENNETT and GERVASE HEWITSON WILLIS.

THE observation that dibenzyl ether may be induced to crystallise below 0°, in spite of a marked tendency to supercooling, afforded us the opportunity to add this substance to the list of available cryoscopic solvents. The pure substance melts at +3·60°. The following values of the cryoscopic constant *K* were found with various solutes: Phenetole 62·6, ethylene dibromide 61·8, dimethylaniline 62·8, naphthalene 63·6. From the mean of these values, 62·7, the latent heat of fusion of dibenzyl ether is calculated to be 24·4 cals. per g.

A few cryoscopic observations were also made with benzoic and acetic acids and benzyl alcohol as solutes. A tendency for ethers to unite with hydroxylic substances to yield complexes of the type $R_2O \longrightarrow HOR'$ (Sidgwick, "The Electronic Theory of Valency,"

p. 137) should show itself by causing the apparent molecular weight of a substance R′OH to be less in solution in the ether R_2O than in a solvent chemically indifferent to it such as benzene, in which association of the hydroxylic substance is likely to be more pronounced. The only ether previously proposed as a cryoscopic solvent is diphenyl ether (Durand and Rougé, *Bull. Soc. chim.*, 1925, **37**, 697), but it is less suitable than dibenzyl ether for testing the point under discussion on account of the lower donating power which is to be expected in an oxygen atom attached directly to the benzene nucleus.

In Table I our values for the apparent molecular weights (*M*) of the hydroxylic substances examined in dibenzyl ether are compared with the values at corresponding concentrations and closely similar temperatures in benzene solution as recorded in the literature (Beckmann, *Z. physikal. Chem.*, 1888, **2**, 729; Auwers, *ibid.*, 1893, **12**, 689). The values for benzoic and acetic acids are definitely lower in dibenzyl ether than in benzene, but those for benzyl alcohol are not appreciably different in the two solvents. The ebullioscopic measurements of Beckmann (*ibid.*, 1890, **6**, 437) show a similar difference in the direction expected.

TABLE 1.

Solute.	*Solvent.*	*Concentration (%).*	*M.*
Benzoic acid.	Benzene.	1·44—4·73	228—236
	Dibenzyl ether.	1·1 —5·3	147—177
Acetic acid.	Benzene.	1·19—4·47	115—122
	Dibenzyl ether.	1·6 —5·0	91·6—109
Benzyl alcohol.	Benzene.	1·57—5·12	116—165
	Dibenzyl ether.	2·0 —4·5	135—140

EXPERIMENTAL.

Preparation and Purification of Dibenzyl Ether.—The ether was conveniently prepared by boiling a mixture of benzyl alcohol (30 g.) and benzyl chloride (25 g.) with potassium hydroxide (25 g.) for 5 hours, and fractionating the product. Repeated distillation under diminished pressure did not eliminate the odour of benzaldehyde. It appears that the ether suffers a slight decomposition in distillation even at temperatures below 200°. After repeated fractional freezing, the substance had b. p. 184°/28 mm., 170°/16 mm., m. p. 3·60°, $d_{4°}^{10·5°}$ (vac.) 1·0504, $d_{4°}^{20°}$ (vac.) 1·0428, and its faint odour was quite distinct from that of benzaldehyde. The liquid often remained for hours in the supercooled state without crystallising spontaneously. Crystallisation could always be induced, however, by vigorous stirring at a temperature below −15°.

Cryoscopic Measurements.—The observations were made with the

Beckmann apparatus, the usual precautions being adopted. Nucleation was always necessary in order to bring about crystallisation of the solvent without undue supercooling. The data obtained with standard substances are recorded in Table II, Δt being the observed depression of the freezing point of dibenzyl ether when w g. of solute were dissolved in 26·10 g. of solvent.

The values with benzil as solute are anomalous. These and the first value for naphthalene have been ignored in taking the mean value of K.

TABLE II.

Solute.	w.	Δt.	K.	Solute.	w.	Δt.	K.
Phenetole	0·5119	1·012°	63·0	Naphthalene	0·3645	0·745°	(68·2)
	0·7493	1·464	62·2		0·9946	1·907	64·1
Ethylene	0·5028	0·621	60·4		1·411	2·662	63·1
dibromide	1·065	1·391	63·9	Benzil	0·6610	0·887	(73·5)
	1·610	2·000	61·0		1·125	1·437	(70·1)
Dimethyl-	0·4153	0·832	63·4		1·646	2·005	(66·7)
aniline	0·8484	1·668	62·1				

THE UNIVERSITY, SHEFFIELD. [*Received, July 2nd*, 1928.]

CCCII.—*Derivatives of 2-Phenyl-6-methyl-4-pyrone. The Non-resolution of 2-Phenyl-6-methyl-4-pyrone* d-α-*Bromocamphor-π-sulphonate.*

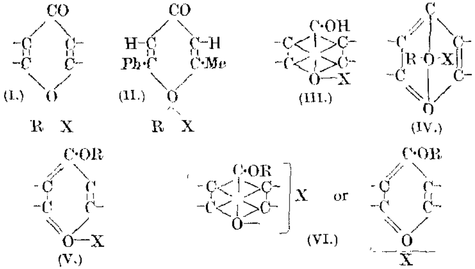
By CHARLES STANLEY GIBSON and JOHN LIONEL SIMONSEN.

IN a note published some years ago (P., 1913, **29**, 159), Levy, Holmyard, and Ruhemann described briefly some experiments on the attempted resolution of the relatively stable 2-phenyl-6-methyl-4-pyrone *d*-α-bromocamphor-π-sulphonate into its diastereoisomerides. Subsequently Dr. Levy continued these experiments in this department, but, finding himself unable to devote the necessary time to the work, he suggested that we should complete the investigation.

At the time of publication of the above note, the authors held the view that the salts of the 4-pyrones were true oxonium salts represented by the general formula (I), where R = H and X = acid radicals, and in this case it is obvious that in derivatives such as (II), which are asymmetrical, resolution of the salt into its diastereoisomerides is to be anticipated.

Since Collie and Tickle (J., 1899, **75**, 710) first described the salts of dimethylpyrone and ascribed to them formula (I), the constitution of these salts has been the subject of much discussion. Werner (*Ber.*, 1901, **34**, 3309) suggested the centric formula (III), whilst Collie (J., 1904, **85**, 971) adopted a bridged formula (IV). The

important experiments of Baeyer (*Ber.*, 1910, **43**, 2337) appeared to show beyond question that the correct formulation of the salts was (V). In 1914, Boon, Wilson, and Heilbron (*J.*, **105**, 2176; compare Baly, Collie, and Watson, *J.*, 1909, **95**, 144), from a study of the absorption spectra of a number of arylidene-pyrones and their salts, suggested that although the salts of dimethylpyrone were best represented by the bridged structure (IV), the salts of the arylidene-bases were true oxonium salts (I).



(I.) (II.) (III.) (IV.) (V.) (VI.)

Hantzsch (*Ber.*, 1919, **52**, 1535, 1544), from a comparison of the absorption spectra of the pyrones, thiopyrones, and their salts, concluded that the true salts were co-ordination compounds of the general formula (VI), which is identical with that (III) suggested by Werner (*loc. cit.*). This view was apparently accepted by Arndt, Scholz, and Nachtwey (*Ber.*, 1924, **57**, 1903). The bridged formula of Collie would, however, appear still to have adherents (compare Drew, this vol., p. 518).

The divergent views on the constitution of the salts of the 4-pyrones enhance the importance of a careful repetition of Levy, Holmyard, and Ruhemann's experiments, since if the resolution of 2-phenyl-6-methyl-4-pyrone *d*-α-bromocamphor-π-sulphonate could be effected, it would lend support to a bridged formulation of these salts, as it would be difficult to account for optical isomerism in the case of co-ordinated compounds. We have therefore subjected the pure salt to a prolonged and careful systematic examination. Seventeen fractional crystallisations from pure dry acetone were carried out, but the optical rotatory powers of the six final fractions, when dissolved in pure ethyl alcohol, were all identical, and no sign of resolution was observed. In so far as one is justified in drawing conclusions from negative results, therefore, our experi-

ments would appear to support the co-ordination formulation of these salts.

As it seemed to us possible that a methylated compound might more readily lend itself to resolution, we prepared the *methylmethosulphate* and the *methiodide* of 2-phenyl-6-methyl-4-pyrone. These compounds were, however, found to be unsuitable, being readily hydrolysed.

It has been suggested by Boon, Wilson, and Heilbron (*loc. cit.*) that the salts of the arylidene-pyrones are true oxonium salts (see, however, Heilbron, Barnes, and Morton, *J.*, 1923, **123**, 2564); we therefore prepared *2-phenyl-6-piperonylidenemethyl-4-pyrone*, but this colourless substance yields such intensely coloured salts that the stereochemical investigation of the d-α-*bromocamphor-π-sulphonate* has so far been found to be impossible with the equipment at present available. When the piperonylidene derivative is treated with bromine in chloroform solution a yellow crystalline solid, m. p. 155—157°, is obtained; this was not analysed but probably consisted of the dibromo-derivative (compare Boon, Wilson, and Heilbron, *loc. cit.*). On crystallisation from acetone, hydrogen bromide was eliminated and an ochreous crystalline solid, m. p. 222°, separated. Analysis showed this to be the *monobromopiperonylidenepyrone* but the position of the bromine atom was not determined.

EXPERIMENTAL.

2-Phenyl-6-methyl-4-pyrone.—The pyrone was prepared by the method of Ruhemann (*J.*, 1908, **93**, 431), except that finely powdered sodamide was used in place of dry sodium ethoxide and the reaction mixture was mechanically stirred during the condensation. By these modifications of the original process the yield was somewhat improved.

The *hydrochloride* was readily obtained by the saturation of an ethereal solution of the pyrone with hydrogen chloride at 0° (Levy, Holmyard, and Ruhemann, *loc. cit.*). The crude salt melted somewhat indefinitely at 161°, and crystallised from a large volume of acetone in fine, glistening prisms, which softened at 105° and melted to a red oil at 165°. It was very readily soluble in water and alcohol, only sparingly soluble in acetone, and insoluble in ether, benzene, and light petroleum (Found: C, 64·7; H, 4·9; HCl, 16·2. $C_{12}H_{11}O_2Cl$ requires C, 64·7; H, 4·9; HCl, 16·4%).

Perchlorate. A warm solution of the pyrone (1 g.) in dilute alcohol (3 c.c.) was treated with an excess of a dilute aqueous solution of perchloric acid. The *perchlorate* separated immediately as an oil which rapidly solidified. It crystallised from dilute alcohol or from much hot water in fine needles, which softened at 135—

137° and melted at 145—147° (Found: C, 61·0, 61·6; H, 4·6; $HClO_4$, by titration, 21·4. $C_{24}H_{21}O_8Cl$ requires C, 61·0; H, 4·5; $HClO_4$, 21·3%).

Sulphate. The pyrone, dissolved in the minimum quantity of methyl alcohol, was treated with the requisite amount of 0·1*N*-sulphuric acid, and the clear solution evaporated to dryness under diminished pressure at room temperature. The crystalline residue after trituration with a little cold acetone had m. p. 165°. It separated from much acetone in iridescent glistening prisms, m. p. 168—169°. It was very soluble in water and methyl alcohol, but insoluble in benzene and ethyl acetate (Found: C, 50·4; H, 4·5. $C_{12}H_{12}O_6S$ requires C, 50·7; H, 4·2%).

Methylmethosulphate. The pyrone, dissolved in the minimum quantity of benzene, was mixed with the calculated amount of freshly distilled methyl sulphate. On standing, the solution, which developed a pink colour, gradually deposited the methylmethosulphate in fine, long needles. After remaining for 48 hours, the crystals were collected, washed with benzene, and dried in a vacuum, m. p. 140—143° with slight previous softening (Found: C, 53·0; H, 5·0. $C_{14}H_{16}O_6S$ requires C, 53·8; H, 5·1%). The *methylmethosulphate* could not be purified by recrystallisation. It was very soluble in water, and in methyl and ethyl alcohols, but insoluble in benzene, ethyl acetate, and light petroleum; it dissolved in a large volume of hot dry acetone, but underwent decomposition. The first fraction which separated on cooling softened at 120° and had m. p. 140—142°, analysis showing it to be a mixture of the methylmethosulphate and the sulphate (Found: C, 51·3; H, 4·9. Calc. for $C_{12}H_{12}O_6S$: C, 50·7; H, 4·2%. Calc. for $C_{14}H_{16}O_6S$: C, 53·8; H, 5·1%). The presence of the sulphate in the solution was confirmed by concentration, whereupon the pure sulphate crystallised in prisms, m. p. 167° (Found: C, 50·2; H, 4·4%). When an aqueous solution of the methylmethosulphate (m. p. 140—143°) was treated with a dilute solution of perchloric acid, the pyrone perchlorate, m. p. 145—147°, was obtained (Found: C, 60·4; H, 4·4; Cl, 7·5. Calc.: C, 61·0; H, 4·5; Cl, 7·5%). The methylmethosulphate did not react with silver *d*-α-bromocamphor-π-sulphonate in alcoholic solution.

Methiodide. When the methylmethosulphate, dissolved in water, was treated with an excess of a dilute solution of potassium iodide, and placed in the ice-chest, the *methiodide* gradually separated. The crystals, which were generally discoloured, decomposed at 105° and were somewhat unstable. Purification was best effected by solution in cold acetone and precipitation by careful addition of light petroleum; colourless needles were deposited, the decom-

position point being unchanged. On keeping, the crystals rapidly become discoloured owing to the liberation of iodine. This compound was analysed by Dr. Levy (Found: C, 47·3; H, 4·1. $C_{13}H_{13}O_2I$ requires C, 47·6; H, 4·0%). The methiodide cannot be prepared by the direct action of methyl iodide on the pyrone; when heated under diminished pressure it decomposed with liberation of methyl iodide and regeneration of the pyrone. The pyrone was also formed when the methiodide was shaken in aqueous solution with either silver oxide or lead oxide. On treatment of an alcoholic solution of the methiodide with perchloric acid, the perchlorate of the pyrone was formed.

2-Phenyl-6-methyl-4-pyrone d-*α-Bromocamphor-π-sulphonate*.—We have prepared this salt by two methods, the second method being preferred for the preparation in quantity, since the pyrone hydrochloride can be more effectively purified than the pyrone itself. (i) The pyrone, dissolved in the minimum quantity of alcohol, was mixed with the requisite amount of a standard aqueous solution of *d*-α-bromocamphor-π-sulphonic acid. When the solution was evaporated to dryness under diminished pressure at room temperature, the salt remained as a crystalline solid. It was recrystallised from acetone and obtained in colourless prisms, m. p. 153—154°.

(ii) The pyrone hydrochloride (10 g.) in alcohol (125 c.c.) was mixed with a solution of silver *d*-α-bromocamphor-π-sulphonate * (18·5 g.) in alcohol (100 c.c.), both solutions being slightly warmed. Silver chloride separated immediately, and after standing for some hours the solution was filtered, and the solvent removed at 30° under diminished pressure, a colourless salt remaining. This was systematically recrystallised from acetone, and after seventeen crystallisations six fractions were obtained. The optical rotatory powers, determined in all cases in absolute ethyl alcohol at 20° ($c = 0·400$, $l = 4$), were: $[\alpha]_{5461}$ +83·05°, 82·7°, 82·6°, 82·5°, 82·35°, 82·2°. The salt crystallised from acetone in colourless prisms, softening at 153°, m. p. 157—158° (Found: C, 52·9; H, 5·2. Calc.: C, 53·1; H, 5·0%).

2-Phenyl-6-piperonylidenemethyl-4-pyrone.—To a mixture of 2-phenyl-6-methyl-4-pyrone (1·6 g.) and piperonal (1·5 g.) in alcohol (5 c.c.), a drop of concentrated potassium hydroxide solution was added. A deep red colour developed, and on standing a crystalline solid (1·4 g.) separated. The *piperonylidene* derivative crystallised from acetone, in which it was somewhat sparingly soluble, in colour-

* This salt does not appear to have been analysed previously. It crystallised from alcohol with one molecule of water of crystallisation (Found: C, 27·3; H, 3·6; Ag, 24·6. $C_{10}H_{14}O_4SBrAg,H_2O$ requires C, 27·5; H, 3·7; Ag, 24·8%).

less, soft needles, m. p. 194° (Found: C, 75·4; H, 4·5. $C_{20}H_{14}O_4$ requires C, 75·4; H, 4·4%). It dissolved in concentrated hydrochloric acid, yielding a deep red solution, the salt being decomposed by addition of water. The *perchlorate*, prepared by the addition of perchloric acid to an acetone solution of the pyrone, crystallised in terra-cotta needles, decomp. 143°. Owing to its exploding just above the m. p., the compound could not be analysed. The salt dissociated somewhat readily and could only be recrystallised in the presence of perchloric acid.

For the preparation of the *d-α-bromocamphor-π-sulphonate*, the piperonylidene derivative (0·4852 g.) was dissolved in hot acetone (90 c.c.), and an aqueous solution of the acid (0·475 g.) added. The orange-coloured solution was evaporated to dryness under diminished pressure at room temperature, and an orange, crystalline solid remained. This was recrystallised from much dry acetone, from which it separated in soft orange prisms, m. p. 205—206° with slight previous softening (Found: C, 57·2; H, 4·7. $C_{30}H_{29}O_8BrS$ requires C, 57·2; H, 4·6%).

When a chloroform solution of the piperonylidene derivative of the pyrone was treated with an equivalent quantity (1 mol.) of bromine, a bright red solid separated. This rapidly redissolved, and on stirring a yellow crystalline solid was deposited. This had m. p. 155—157°, but unfortunately it was not analysed. On recrystallisation from acetone, in which it was sparingly soluble, it apparently underwent decomposition with loss of hydrogen bromide, and the *monobromo*-derivative separated in ochreous plates, decomp. 222°. The quantity available was insufficient for the determination of the position of the bromine atom (Found: Br, 19·9. $C_{20}H_{13}O_4Br$ requires Br, 20·1%).

We wish to acknowledge the assistance of Dr. J. H. Nutland who prepared some of the pyrone used in these experiments and carried out some of the analyses. A grant from the Government Grant Committee of the Royal Society, which has covered the greater portion of the cost of this investigation, is also gratefully acknowledged.

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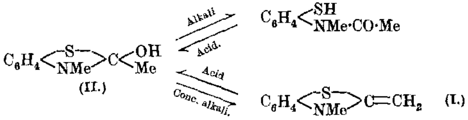
CCCIII.—*The Methylene Bases from 1-Methylbenzthiazole and 1-Methylbenzselenazole Methiodides; with a Note on the Preparation of 1-Substituted Benzthiazoles.*

By LESLIE MARSHALL CLARK.

1-METHYLBENZTHIAZOLE methiodide reacts with ammonium hydroxide in dilute aqueous solution, yielding as the main product the ammonium salt of *o*-acetmethylamidothiophenol, since atmospheric oxidation of the solution gives 2 : 2′-diacetmethylamidodiphenyl disulphide (J., 1925, **127**, 973). König and Meier (*J. pr. Chem.*, 1925, **109**, 324) have shown that when 1-methylbenzthiazole methoperchlorate is suspended in acetone and shaken with concentrated sodium hydroxide solution, the acetone extracts a base which they identify as 2-methyl-1-methylenebenzthiazoline (I).

Further examination of the reaction with ammonia and with dilute sodium hydroxide proves that a certain amount of the methylene base is produced in either case, whilst in the latter case the proportion of methylene base to thiophenol is increased by increasing the alkali concentration. It is evident, therefore, that the carbinol (II) decomposes in the presence of alkali in the two directions :



When the compound (I) is heated in alcoholic hydrogen chloride solution or when alkali salts of *o*-acetmethylamidothiophenol are acidified, 1-methylbenzthiazolinium salts result. Each of the directions of reaction in which the carbinol base can decompose under the influence of alkalis is therefore reversible in the presence of acids.

Since quaternary salts in the benzselenazole series react with alkalis to give products similar to those obtained from the analogous benzthiazolinium salts (J., 1927, 2805), the behaviour of 1-*methylbenzselenazole methiodide* has also been investigated. The base could not be obtained by the action of acetic acid on the zinc salt of *o*-aminoselenophenol, the products of this reaction being selenium and acetanilide, but was readily formed by condensation of the zinc salt with acetyl chloride. The methiodide in aqueous solution reacts

immediately with dilute sodium hydroxide giving *2-methyl-1 methylenebenzselenazoline* together with the sodium salt of *o*-acety: methylaminoselenophenol.

The course of the reaction may be followed by titration wit phenolphthalein as indicator, part of the methiodide yielding precipitate of the selenazoline (and consequently neutralising on equivalent of alkali), whilst the remainder is converted into th neutral sodium salt of the selenophenol (at the same tim neutralising 2 equivs. of alkali). A much higher proportion of th methylene base is formed with 1-methylbenzselenazole methiodid than with the analogous sulphur compound. 2-Methyl-1-methylene benzselenazoline, like its sulphur analogue, is reconverted into th ammonium salt by heating with alcoholic hydrogen chloride.

Mills and Raper (J., 1925, **127**, 2466) have isolated the highly coloured condensation product obtained by reaction of *p*-dimethyl aminobenzaldehyde with the reactive methylene group in 1-methyl 2-methylene-1 : 2-dihydro-β-naphthaquinoline. The aldehyde con denses similarly with 2-methyl-1-methylenebenzthiazoline in alcohol giving a deep red solution from which no solid material could b isolated. The solution evidently contains the compound (III) since on addition of one mol. of hydriodic acid, *p*-dimethylamino styrylbenzthiazole methiodide (IV) is formed, addition of the aci evidently taking place in a manner analogous to that described b Mills and Raper (*loc. cit.*).

$$C_6H_4<{}^{S}_{NMe}>C:C:CH\cdot C_6H_4\cdot NMe_2 \quad (III.)$$

$$C_6H_4<{}^{S}_{N(Me)I}>C\cdot CH:CH\cdot C_6H_4\cdot NMe_2 \quad (IV.)$$

The presence of the reactive methyl group in 1-methylbenz selenazole methiodide suggested that selenocarbocyanine formatior might be possible. By using the general method of preparation o carbocyanines described by Hamer (J., 1927, 2796), *i.e.*, the con densation in pyridine solution of orthoformic ester with the meth iodides of bases containing a reactive methyl group, good yields o both 2 : 2′-*dimethyl*- and 2 : 2′-*diethylselenocarbocyanine iodides* (V) were obtained. Like the thiocarbocyanines described by Mill (J., 1922, **121**, 455), these compounds are powerful sensitisers of th photographic plate.

$$C_6H_4<{}^{Se}_{N(R)I}>C\cdot CH:CH\cdot CH:C<{}^{Se}_{N(R)}>C_6H_4 \quad (V.)$$

In *C*-substituted benzoxazoles, fission of the heterocyclic ring is increasingly difficult to bring about as the volume and valency demands of the substituent group increase (Skraup, *Annalen*, 1919, **419**, 1). The influence of the *C*-phenyl group, although well-marked in the benzoxazole series, is insufficient in the benzthiazolinium series to make possible the isolation of a carbinol base of the type (*II*), even when silver hydroxide is used instead of sodium hydroxide (J., 1925, **127**, 973) as basifying agent.

The well-known Hofmann synthesis of 1-substituted benzthiazoles (*Ber.*, 1880, **13**, 21), whereby *o*-aminothiophenol is heated with the appropriate acid, acid anhydride, or acid chloride, is not entirely satisfactory. An alternative method is therefore described. 2 : 2′-Diaminodiphenyl disulphide is acylated by treatment with the appropriate acid or acid chloride, and this compound is reduced with sodium hydrosulphite yielding the acylamino-thiophenol, which condenses with elimination of water to give the 1-substituted benzthiazole (compare Clark, *loc. cit.*, and Phillips, this vol., p. 172).

EXPERIMENTAL.

2-Methyl-1-methylenebenzthiazoline is formed in small yield by the action of ammonia, silver hydroxide, or *N*-sodium hydroxide on 1-methylbenzthiazole methiodide in aqueous solution. The maximum yield was obtained by the following modification of König and Meier's method (*loc. cit.*). The methiodide (4 g.) was suspended in acetone and shaken with 50% sodium hydroxide solution. When no quaternary salt remained undecomposed, the acetone solution was evaporated and the pinkish residue extracted with toluene (5 c.c. and 2 c.c.). A small quantity of dark red oil, which afterwards solidified, remained undissolved; this was separated by acetone into a sparingly soluble, dark red, crystalline substance and a colourless substance which separated in needles, m. p. 164°. These compounds were not further examined. The toluene solution, when cooled, deposited 0·81 g. of stout, colourless tablets of 2-methyl-1-methylenebenzthiazoline, m. p. 170° (König and Meier give 164°) (Found: C, 66·2; H, 5·6; N, 8·7. Calc.: C, 66·3; H, 5·5; N, 8·6%). A mixture of this substance with 2 : 2′-diacetmethylamidodiphenyl disulphide, m. p. 171°, melted at 128°. When these two compounds are heated together they develop a brilliant red colour.

By the action of benzoyl chloride on a solution of the sodium salt of *o*-acetmethylamidothiophenol, the *benzoyl* derivative was obtained; from light petroleum it separated in colourless needles, m. p. 87° (Found: C, 67·0; H, 5·2. $C_{16}H_{15}O_2NS$ requires C, 67·4; H, 5·3%).

1-*Methylbenzthiazole methopicrate*, prepared from the methiodide

and picric acid, separated from aqueous solution in yellow needles which, when kept in a vacuum over sulphuric acid, became liquid and then resolidified. It then had m. p. 94° (Found: N, 14·7. $C_{15}H_{12}O_7N_4S$ requires N, 14·3%). The *hydrogen sulphate* separated from alcohol–ether in colourless needles, m. p. 177—178° (Found: SO_4, 38·5. C_8H_7NS,H_2SO_4 requires SO_4, 38·75%); the *methochloroplatinate*, prepared from the methochloride and chloroplatinic acid in alcoholic solution, separated in deep yellow crystals, m. p. 224° (decomp.) [Found: Pt, 26·2. $(C_9H_{10}NS)_2PtCl_6$ requires Pt, 26·5%]; the *perchlorate* separated from alcohol–ether in colourless needles, m. p. 149°, and exploded during combustion.

Action of Silver Hydroxide on 1-*Phenylbenzthiazole Methiodide.*—The methiodide (2 g.), dissolved in water (35 c.c.) and acetone (50 c.c.), was shaken for an hour with excess of silver hydroxide; the filtrate from the insoluble material contained none of the expected 1-hydroxy-1-phenyl-2-methylbenzthiazoline, the major portion of the thiazole compound being mixed with the silver oxide and iodide residue, probably as the silver salt of *o*-benzoylmethylaminothiophenol (compare Mills, Clark, and Aeschlimann, J., 1923, **123**, 2353). The sodium salt of *o*-benzoylmethylaminothiophenol was benzoylated by shaking with benzoyl chloride, and the *benzoyl* derivative, when crystallised from light petroleum, had m. p. 130—131° (Found: C, 72·6; H, 4·8. $C_{21}H_{17}O_2NS$ requires C, 72·6; H, 4·85%).

For the characterisation of 1-phenylbenzthiazole quaternary salts, the following compounds were prepared by the usual methods: 1-*Phenylbenzthiazole methochloroplatinate*, m. p. 243° (decomp.) [Found: Pt, 22·7. $(C_{14}H_{12}NS)_2PtCl_6$ requires Pt, 22·7%]; *methopicrate*, orange-yellow plates, m. p. 125—126° (Found: N, 12·4. $C_{20}H_{14}O_7N_4S$ requires N, 12·3%); *methoperchlorate*, colourless needles, m. p. 220° (Found: S, 10·0. $C_{14}H_{12}O_4NSCl$ requires S, 9·8%).

Preparation of 1-*Methylbenzselenazole.*—A preliminary experiment on the action of glacial acetic acid (150 c.c.) on the zinc salt of *o*-aminoselenophenol (17 g.) in an atmosphere of carbon dioxide showed that selenium was deposited; the only product which could be isolated from the filtrate was acetanilide, m. p. 114° (Found: C, 71·35; H, 6·1; N, 10·4. Calc.: C, 71·1; H, 6·7; N, 10·4%). When the acetic acid was replaced by acetyl chloride, the condensation took place smoothly: The zinc salt (7 g.) was suspended in benzene (50 c.c.), and acetyl chloride in excess (10 c.c.) was added slowly with constant shaking; the brown oil which separated solidified after 16 hours. The reaction mixture was heated on the water-bath for 1 hour and cooled. Water and excess of ammonia

were then added. The solid slowly dissolved, and the benzene layer was separated. The aqueous solution was extracted with ether, the combined organic extracts were dried over sodium carbonate, and most of the solvent was distilled off. Addition of light petroleum then precipitated a yellowish gum, which was probably 2 : 2′-diacetamidodiphenyl diselenide, but which was not investigated. The solution was removed and concentrated, and the residual oil distilled under reduced pressure. 1-*Methylbenzselenazole* (4·6 g.) was thus obtained as an almost colourless liquid, b. p. 140°/51 mm. It was analysed as the *chloroplatinate*, which separates from alcoholic solutions in yellow needles [Found : C, 24·4 ; H, 1·95 ; Pt, 24·6. $(C_8H_7NSe)_2,H_2PtCl_6$ requires C, 23·9 ; H, 2·0 ; Pt, 24·4%). The *methiodide*, obtained by heating the base (3·8 g.) with methyl iodide (6 g.) at 100° for 8 hours, crystallised from alcohol in fine, colourless needles, m. p. 221° (decomp.); yield, 5·5 g. (Found : I, 37·4 ; Se, 23·6. $C_9H_{10}NISe$ requires I, 37·6 ; Se, 23·4%) ; and the *ethiodide*, similarly obtained by 16 hours' heating, crystallised from alcohol in colourless, flattened needles, m. p. 212° (decomp.) (Found : I, 35·9. $C_{10}H_{12}NISe$ requires I, 36·1%). The *methochloroplatinate*, prepared from the methochloride in the usual way, had m. p. 214° (decomp.) [Found : Pt, 23·1. $(C_9H_{10}NSe)_2PtCl_6$ requires Pt, 22·9%].

Action of Sodium Hydroxide on 1-*Methylbenzselenazole Methiodide.*—Addition of *N*/20- or *N*-sodium hydroxide solution to aqueous solutions of the methiodide causes the formation of a voluminous, curdy, pale yellow precipitate of 2-*methyl*-1-*methylenebenzselenazoline*, which crystallises from its orange-red alcoholic solution in pale yellow plates, m. p. 157—158° (Found : C, 51·4 ; H, 4·4 ; N, 7·1. C_9H_9NSe requires C, 51·4 ; H, 4·3 ; N, 6·7%). The compound is sparingly soluble in alcohol and shows a tendency to form a brown mass when warmed with that solvent. From 1 g. of the methiodide, 0·346 g. of methylene base (dried over sulphuric acid) was obtained, and the change of titre was 4·0 c.c. of *N*-alkali ; if the reaction proceeded as suggested on p. 2314, the change of titre should have been 4·3 c.c. The alkaline solution, after removal of the methylene base, was oxidised with potassium ferricyanide and gave an oily suspension which rapidly crystallised. The solid product, 2 : 2′-*diacetmethylamidodiphenyl diselenide*, crystallised from petroleum ether in colourless flat needles, m. p. 141° (Found : C, 47·3 ; H, 4·4 ; N, 6·3. $C_{18}H_{20}O_2N_2Se_2$ requires C, 47·6 ; H, 4·4 ; N, 6·2%).

Reversibility of Methylene-base Formation in the Benzthiazole and Benzselenazole Series.—(1) *Action of hydrochloric acid on* 2-*methyl*-1-*methylenebenzthiazoline*. The methylene base (0·2 g.) in alcohol

(5 c.c.) was heated under reflux with hydrochloric acid (2 c.c.) fc 2 hours. Addition of chloroplatinic acid then caused the separatio of yellow needles which slowly disappeared as a heavy, brown crystalline deposit was formed. This compound had m. p. 224 (decomp.), not depressed when mixed with authentic 1-methy benzthiazole methochloroplatinate (Found : Pt, 26·2. Calc. Pt, 26·5%).

(2) *Action of hydrochloric acid on 2-methyl-1-methylenebenz selenazoline.* The reaction was carried out as for the sulphur com pound, the chloroplatinate separating from the alcoholic solution i stout, yellowish-brown needles, m. p. 214° (decomp.) (Found Pt, 23·1. Calc. : Pt, 22·9%), not depressed by admixture wit 1-methylbenzselenazole methochloroplatinate.

Condensation of 2-Methyl-1-methylenebenzthiazoline with p-*Di methylaminobenzaldehyde.*—Dimethylaminobenzaldehyde and th methylene base (0·71 g. of each) were heated in alcoholic solutio (15 c.c.) for 1 hour. An intense red colour developed, but no soli material separated when the mixture was cooled and kept fo 12 hours. To the hot solution, therefore, hydriodic acid (*d* 1·7 1·1 c.c., 1 mol.) was added. The purple, crystalline precipitate wit bronze reflex, which separated on cooling, was easily soluble i alcohol, and was crystallised from that solvent containing a littl sulphurous acid; *p*-dimethylaminostyrylbenzthiazole methiodid (Found : S, 7·6. Calc. : S, 7·6%) melted at 244—245°, unchange by admixture with an authentic specimen, m. p. 245°, prepared b Dr. F. M. Hamer from 1-methylbenzthiazole methiodide and th aldehyde. The absorption spectra in alcohol of the two samples ar identical, showing maxima at λ 4350 and λ 6400.

Condensation of Orthoformic Ester with 1-Methylbenzselenazol Methiodide.—The methiodide (1·45 g.) and orthoformic este (1·5 c.c.) were boiled in dry pyridine solution (15 c.c.) for 1 hour. A deep purple colour rapidly developed, and a crystalline deposit wa formed. The mixture was poured into water and kept for 12 hours 2 : 2′-*Dimethylselenocarbocyanine iodide*, thus obtained, wa crystallised from ethyl alcohol (1·3 l.), and separated from the ho deep red solution in flocculent masses of fine, bronze needles, m. p 267—268° (decomp.); yield 0·8 g. (Found* : C, 40·5; H, 3·5; N, 4·8 $C_{19}H_{17}N_2ISe_2$ requires C, 40·8; H, 3·0; N, 5·0%). In alcoholi solution the dye has absorption maxima at λ 4500 and λ 6400, whils it confers sensitivity on a bathed plate up to λ 7020.

Condensation of Orthoformic Ester with 1-Methylbenzselenazol Ethiodide.—The condensation was carried out in the manne described for the methyl compound. The yield of 2 : 2′-*diethyl*

* Microanalysis by H. Weil, Munich.

selenocarbocyanine iodide from 0·5 g. of 1-methylbenzselenazole ethiodide was 0·27 g. The solubility of the higher homologue is considerably greater than that of the lower, since this amount of dye could be crystallised from 50 c.c. of alcohol. It separates in *glistening, dark green needles*, m. p. 270—271° (decomp.) (Found *: N, 4·8. $C_{21}H_{21}N_2ISe_2$ requires N, 4·8%). The absorption spectrum in alcoholic solution shows maxima at λ 4500 and λ 6420. The sensitivity band of a bathed plate has a slight maximum at λ 6200, falling off steeply to the red at λ 6940.

The Preparation of 1-Substituted Benzthiazoles.

2 : 2′-*Diacetamidodiphenyl disulphide* was prepared by boiling 2 : 2′-diaminodiphenyl disulphide (8·0 g.) with glacial acetic acid (50 c.c.) and acetic anhydride (10 c.c.) for 5 hours. Dilution of the solution and neutralisation with ammonia precipitated a colourless oil, which rapidly crystallised (9·3 g.): when recrystallised from ethyl acetate, it separated in masses of colourless, flocculent needles, m. p. 165—166° (Found : N, 8·4. $C_{16}H_{16}O_2N_2S_2$ requires N, 8·4%), readily soluble in alcohol.

1-*Methylbenzthiazole*.—2 : 2′-Diacetamidodiphenyl disulphide (12·2 g.) was dissolved in hot aqueous alcohol, and excess of solid sodium hydrosulphite (15 g.) was added in three portions. Heating was continued during 15 minutes. After the addition of hydrochloric acid (35 c.c.) the solution was concentrated on the water-bath. Basification with sodium hydroxide solution precipitated an oily paste which was extracted with ether. The ethereal solution was dried over sodium carbonate and evaporated, leaving 3·5 g. of a yellow oil, which, on distillation under reduced pressure, yielded 2·0 g. of pure 1-methylbenzthiazole, identified by means of its picrate, m. p. 155—156°, identical with that obtained from an authentic specimen.

2 : 2′-*Dipropionamidodiphenyl disulphide* was obtained by boiling 2 : 2′-diaminodiphenyl disulphide (6 g.) for 12 hours with propionic acid (50 g.); the disulphide was precipitated as a dark brownish oil on dilution and neutralisation of the acid solution, but solidified on standing over-night. A portion, washed with ether and crystallised from light petroleum (b. p. 60—80°), separated in colourless, flocculent masses, m. p. 138° (Found: N, 7·95. $C_{18}H_{20}O_2N_2S_2$ requires N, 7·8%).

1-*Ethylbenzthiazole*.—Reduction of the foregoing unpurified solid with sodium hydrosulphite as described above for the acetyl compound eventually gave a small quantity of dark-coloured oil. This was not distilled, but 1·6 g. of a picrate were obtained from it by addition of a saturated solution of picric acid in alcohol; after

* Microanalysis by H. Weil, Munich.

recrystallisation from alcohol (charcoal), *1-ethylbenzthiazole picrate* had m. p. 138° (Found: C, 45·8; H, 3·0; N, 14·1. $C_{15}H_{12}O_7N_4S$ requires C, 45·9; H, 3·05; N, 14·3%).

2 : 2'-Dibenzamidodiphenyl Disulphide.—This was obtained in good yield by the Schotten–Baumann method from the base; it crystallised from alcohol, in which it is sparingly soluble, in pale yellow plates, m. p. 143—144·5° (Found: N, 6·3. $C_{26}H_{20}O_2N_2S_2$ requires N, 6·1%).

Reduction. The disulphide (1·2 g.) was dissolved in aqueous acetone, and an excess of sodium hydrosulphite added. The mixture was kept hot for 5 minutes. Hydrochloric acid (10 c.c.) was added and the acetone evaporated. Basification with ammonia precipitated a colourless oil which immediately crystallised. The solid, which when heated had the geranium-like odour characteristic of 1-phenylbenzthiazole, was crystallised from aqueous alcohol, and separated in long needles, m. p. 113°, showing no depression on admixture with an authentic specimen of 1-phenylbenzthiazole; yield 0·9 g.

Preparation of 2 : 2'-Diaminodiphenyl Disulphide.—The method described by Hofmann (*Ber.*, 1894, **27**, 2808) for the preparation of this compound is not satisfactory. Most of the material used in carrying out the above work was prepared by the method of Möhlau (*Ber.*, 1912, **45**, 131). Dr. F. M. Hamer, of Ilford Ltd., kindly prepared 10 g. of the disulphide by Hofmann's method and to her I am indebted for the following note: "After heating aniline (120 g.) and sulphur (35 g.) according to Hofmann's directions, 67% of the aniline was recovered unchanged by steam distillation. From the residue, 400 c.c. of hydrochloric acid (8%) extracted a mixture of bases. The hydrochlorides left on evaporation of this solution were separated by extraction with 400 c.c. of hot water. The sparingly soluble residue was the hydrochloride of a base which had m. p. 81° and was probably 4 : 4'-diaminodiphenyl disulphide. The hot aqueous solution deposited a hydrochloride which on basification gave 5 g. of 2 : 2'-diaminodiphenyl disulphide, m. p. 93°."

I wish to thank Messrs. Ilford Ltd. for the gift of 2 : 2'-diaminodiphenyl disulphide, and for examining the optical and photographic properties of the sensitisers described in this paper. My thanks are due to Dr. F. M. Hamer for the loan of a specimen of *p*-dimethylaminostyrylbenzthiazole methiodide.

NORTH VIEW, NORTHWICH RD.,
WEAVERHAM, NORTHWICH. [*Received, June 29th,* 1928.]

CCCIV.—*The Effects of the Spatial Position of Substituent Groups on Acidic Strength.*

By DONALD HOLROYDE HEY.

IN an investigation on the rotatory powers of a number of the homologous menthyl alkyloxyacetic and hydrogen dicarboxylic esters (Rule, Hay, and Paul, this vol., p. 1347), it was observed that the maxima in the rotation curves of the one series corresponded to the minima in the other. From these results it was concluded that the terminal alkyloxy- and carboxy-groups of the growing chains give rise to opposite changes in rotatory power when they return to the neighbourhood of the asymmetric atom, and, further, that the characteristic influence of *o*-substituents in the optically active benzoic esters is propagated through space rather than through the chain of intervening atoms. In support of these conclusions the authors observed that parallel phenomena may be found in the influence of substituents on the acidity of geometrically isomeric acids.

There appears, however, to be little justification for this generalisation, and available data on the dissociation constants of acids of the type of crotonic acid (as well as of other acids) show that it is not possible to correlate the two phenomena. Recent work on the configuration of the crotonic acids, both from the chemical and physical standpoint, shows that crotonic acid (m. p. 72°) has the *trans*-configuration (Errera and Henri, *Compt. rend.*, 1925, **181**, 548; Langseth, *Z. physikal. Chem.*, 1925, **118**, 49; Auwers and Wissebach, *Ber.*, 1923, **56**, 715). The dissociation constants of the two crotonic acids, and of other acids of the same type on which there is now little doubt with regard to their configuration, are given below:

$CH_3\cdot C\cdot H$ ‖ $H\cdot C\cdot CO_2H$	$H\cdot C\cdot CH_3$ ‖ $H\cdot C\cdot CO_2H$	$Cl\cdot C\cdot CH_3$ ‖ $H\cdot C\cdot CO_2H$	$CH_3\cdot C\cdot Cl$ ‖ $H\cdot C\cdot CO_2H$
Crotonic acid, $0{\cdot}22 \times 10^{-4}$.	*iso*Crotonic acid, $0{\cdot}36 \times 10^{-4}$.	β-Chloro*iso*crotonic acid, $0{\cdot}95 \times 10^{-4}$.	β-Chlorocrotonic acid, $1{\cdot}44 \times 10^{-4}$.
$CH_3\cdot C\cdot H$ ‖ $CH_3\cdot C\cdot CO_2H$	$H\cdot C\cdot CH_3$ ‖ $CH_3\cdot C\cdot CO_2H$	$CH_3\cdot C\cdot H$ ‖ $Cl\cdot C\cdot CO_2H$	$H\cdot C\cdot CH_3$ ‖ $Cl\cdot C\cdot CO_2H$
Tiglic acid, $0{\cdot}09 \times 10^{-4}$.	Angelic acid, $0{\cdot}50 \times 10^{-4}$.	α-Chlorocrotonic acid, $7{\cdot}2 \times 10^{-4}$.	α-Chloro*iso*crotonic acid, $15{\cdot}8 \times 10^{-4}$.

The dissociation constants of the above acids indicate that the spatial proximity of a CH_3 or Cl group to the carboxyl group in every case increases the acidic strength, and that the change thus pro-

duced is in the same direction as (though smaller in magnitude than) that produced by the carboxyl group in fumaric and maleic acids ($K = 10 \times 10^{-4}$ and 150×10^{-4} respectively). From these observations it will be seen that it is not possible to adduce corroborative evidence from this source as claimed by Rule, Hay, and Paul, who infer that the spatial proximity of a CH_3 or Cl group to the carboxyl group produces a lowering of the dissociation constant, *i.e.*, an effect in the opposite direction to that produced by the carboxyl group. The analogy between the two phenomena cited by them is therefore invalid.

The increase in the acidic strength of these acids by the spatial proximity of substituents is in close conformity with the behaviour of substituted benzoic acids, and it is possible to observe a close analogy between the effect of *o*-substitution, which is known always to increase the strength of a benzoic acid independently of the polar character of the substituent, and *cis*-substitution, which is seen to have an effect of the same type on acids of the acrylic acid series. In both cases the increase may be attributed to steric inhibition to the return of the hydrogen ion.

In the case of ortho-substituted benzoic acids (*i.e.*, β-substitution), *the increase in the dissociation constant is considerably greater than* the increase in the corresponding β-substituted aliphatic acids, due *to the superimposed secondary effect of the spatial proximity of the* groups. On the other hand, with the meta- and para-acids, the increase is in nearly every case of the same order of magnitude as is met with in corresponding γ- and δ-substituted acids of the aliphatic series. This is clearly illustrated in the following table of dissociation constants (taken from Landolt–Börnstein, " Tabellen ").

Benzoic acid, $K \times 10^4 = 0{\cdot}66$.

Acid.	$K \times 10^4$.	Acid.	$K \times 10^4$.	Acid.	$K \times 10^4$.
o-Chlorobenzoic	13·0	*m*-Chlorobenzoic	1·5	*p*-Chlorobenzoic	0·93
o-Bromobenzoic	14·5	*m*-Bromobenzoic	1·37	*p*-Bromobenzoic	0·59
o-Hydroxybenzoic	*10·0*	*m-Hydroxybenzoic*	*0·83*	*p-Hydroxybenzoic*	*0·29*
Phthalic	12·0	Homophthalic	2·9	Terephthalic	—
o-Toluic	1·2	*m*-Toluic	0·56	*p*-Toluic	0·43

Propionic acid, $K \times 10^4 = 0{\cdot}14$.

β-Chloropropionic	0·85	γ-Chlorobutyric	0·3	δ-Chlorovaleric	0·204
β-Bromopropionic	0·98	γ-Bromobutyric	0·26	δ-Bromovaleric	0·191
β-Hydroxypropionic	0·31	γ-Hydroxybutyric	0·19	δ-Hydroxyvaleric	0·2
Succinic	0·66	Glutaric	0·47	Adipic	0·37
Butyric	*0·148*	*Valeric*	*0·18*	*Caproic*	*0·145*

With the ortho-substituted acids, the configuration of the molecule is such that the substituent group is permanently maintained at an effective distance from the carboxyl group, and the resulting spatial proximity of the groups is shown in the abnormal increase in the dissociation constant. From these considerations, it would be

expected that *cis*-substitution in like manner would result in an increase in dissociation constant (when compared with *trans*-substitution), and if the new configurations for the crotonic acids are accepted, this analogy is borne out in fact.

UNIVERSITY COLLEGE, SWANSEA. [*Received, June 21st*, 1928.]

CCCV.—*The Intermolecular Condensation of Styryl Ketones. Part II. Styryl Nonyl Ketone and the Formation of Dimerides.*

By ISIDOR MORRIS HEILBRON and FRANCIS IRVING.

IN a previous communication (Dickinson, Heilbron, and Irving, J., 1927, 1888), it was shown that certain styryl methyl ketones on treatment with alkali underwent intermolecular condensation with formation of *cyclo*hexenones, whilst treatment with piperidine resulted in the formation of saturated dimerides, probably of *cyclo*butane structure. We have now extended the investigation to a series of styryl nonyl ketones, and in no case has the formation of *cyclo*hexenones been observed, but a number of saturated dimerides have been obtained by the action of alkali.

Methyl nonyl ketone has previously been condensed with benzaldehyde by means of 0·25% alcoholic potassium hydroxide (Carette, *Compt. rend.*, 1900, **131**, 1225), the product being the simple styryl nonyl ketone, m. p. 41—42°. Carette also discovered that by employing hot 1% alcoholic potassium hydroxide, a dimeride melting at 116° was obtained. Styryl nonyl ketone itself on similar treatment was found to yield the same dimeride.

Scholtz and Meyer (*Ber.*, 1910, **43**, 1861) by means of alkali condensed anisaldehyde, piperonal, *p*-tolualdehyde, and cuminal with methyl nonyl ketone, claiming to have obtained the monomeric styryl nonyl ketones in each case. A re-examination of their products has proved, as could be inferred from their high melting points, that the condensation products from *p*-tolualdehyde and cuminal are actually dimerides.

We have further found that whereas *p*-methoxy-, 3 : 4-dimethoxy-, 3 : 4-methylenedioxy-, and *p*-chloro-styryl nonyl ketones are formed when cold, dilute, aqueous alkali or piperidine is used as condensing agent, dimerides are produced by increasing the alkali concentration and preferably carrying out the reaction on the steam-bath instead of at room temperature. *o*- and *m*-Chloro- and *m*-methoxy-benzaldehydes, *o*-tolu- and salicyl-aldehydes did not yield dimerides when treated under such conditions, and it would

appear that dimeric forms are more readily produced when the aldehyde is substituted in the para-position.

The dimerides are all colourless substances which react as saturated compounds and are extremely inert towards ketone reagents. Carette (*J. Pharm.*, 1901, **13**, 412) found that bis-(styryl nonyl ketone) failed to react with semicarbazide. We have confirmed this observation, but have succeeded in obtaining a *monoxime* from this compound by prolonged treatment with hydroxylamine. This same inactivity has been noted by Stobbe and Hensel (*Ber.*, 1926, **59**, 2254), who only succeeded in obtaining a monoxime from the dimeride of phenyl 4-methoxystyryl ketone. These dimerides doubtless possess a *cyclo*butane structure similar to the products obtained by the action of short wave-length light or piperidine on unsaturated ketones (Stobbe and Hensel, *loc. cit.*).

EXPERIMENTAL.

Styryl Nonyl Ketone.—Benzaldehyde (2·5 g.) and methyl nonyl ketone (4 g.) were mixed with alcohol (2 c.c.), and piperidine (3 drops) was added. The solution was allowed to stand for several days, small amounts of piperidine being added daily; finally, it was diluted and cooled in a freezing mixture, crystals of styryl nonyl ketone then separating. These were recrystallised from methyl alcohol, appearing in colourless leaflets, m. p. 44° (Carette gives 41—42°; Thoms, *Ber. Deut. pharm. Ges.*, 1901, **11**, 3, gives 44—45°).

Monoxime of Bis-(Styryl Nonyl Ketone).—Bis-(styryl nonyl ketone) (1 mol.), prepared according to the method of Carette (*Compt. rend.*, *loc. cit.*), was refluxed with hydroxylamine (2 mols.) for 2 hours in alcoholic solution, and the product recrystallised from alcohol, fine, colourless needles of the *monoxime* being obtained, m. p. 125—126° (Found: N, 2·7. $C_{36}H_{53}O_2N$ requires N, 2·6%).

Bis-(4-methoxystyryl Nonyl Ketone).—Anisaldehyde (3·2 g.) and methyl nonyl ketone (4 g.) were refluxed for 6 hours with 1% alcoholic potassium hydroxide solution (30 g.). The product was repeatedly crystallised from alcohol, being finally obtained in the form of colourless needles, m. p. 120° [Found: C, 79·3; H, 9·4; *M* (Pregl), 474. $C_{38}H_{56}O_4$ requires C, 79·2; H, 9·7%; *M*, 576]. 4-Methoxystyryl nonyl ketone (Scholtz and Meyer, *loc. cit.*) crystallises in colourless leaflets, m. p. 63°.

3 : 4-*Dimethoxystyryl Nonyl Ketone.*—Veratraldehyde (4 g.) and methyl nonyl ketone (4 g.) were dissolved in alcohol (10 c.c.) together with 2 c.c. of 8% sodium hydroxide solution. Crystals separated after 12 hours, and were purified by recrystallisation from methyl alcohol, a small amount of less soluble dimeride being removed during the process. The *ketone* forms faintly yellow, rhombic plates,

m. p. 61° (yield, 5·5 g.) [Found: C, 75·4; H, 9·5; *M* (Menzies), 314, (Pregl), 323. $C_{20}H_{30}O_3$ requires C, 75·4; H, 9·4%; *M*, 318].

Bis-(3 : 4-dimethoxystyryl Nonyl Ketone).—Veratraldehyde (4 g.) and methyl nonyl ketone (4 g.) were refluxed with 1% alcoholic potassium hydroxide (25 g.) for 4 hours. The crude product was repeatedly recrystallised from alcohol, separating in colourless needles, m. p. 135° [Found: C, 75·5; H, 9·2; *M* (Menzies), 646. $C_{40}H_{60}O_6$ requires C, 75·4; H, 9·4%; *M*, 636].

Bis-(3 : 4-methylenedioxystyryl Nonyl Ketone).—Piperonal (4 g.) and methyl nonyl ketone (4 g.) were refluxed with 2% alcoholic potassium hydroxide (40 c.c.) for 6 hours. The product which separated on cooling was repeatedly crystallised from alcohol, and obtained finally in fine, colourless needles, m. p. 128° [Found: C, 75·6; H, 8·5; *M* (Menzies), 608. $C_{38}H_{52}O_6$ requires C, 75·5; H, 8·6%; *M*, 604]. Scholtz and Meyer (*loc. cit.*) describe 3 : 4-methylenedioxystyryl nonyl ketone as forming pale yellow needles, m. p. 56°.

Bis-(4-methylstyryl Nonyl Ketone).—This was first prepared by Scholtz and Meyer (*loc. cit.*) by the addition of 15% sodium hydroxide solution to an alcoholic solution of *p*-tolualdehyde and methyl nonyl ketone, and allowing the solution to stand at room temperature. These authors, however, described the compound as 4-methylstyryl nonyl ketone, m. p. 129°. We have prepared the compound by a similar method, but find it to melt at 134—135° [Found: *M* (Pregl), 425. $C_{38}H_{56}O_2$ requires *M*, 544].

4-iso*Propylstyryl Nonyl Ketone.*—Cuminaldehyde (2 g.) and methyl nonyl ketone (2·5 g.) were dissolved in alcohol (5 c.c.), and 6 drops of 8% sodium hydroxide added. After 2 days, the solution was cooled in ice and salt, and the separated product recrystallised from methyl alcohol, appearing as colourless plates, m. p. 40° [Found: C, 83·9; H, 10·9; *M* (Pregl), 297. $C_{21}H_{32}O$ requires C, 84·0; H, 10·7%; *M*, 300].

*Bis-(4-*iso*propylstyryl Nonyl Ketone).*—This compound was obtained by Scholtz and Meyer (*loc. cit.*) by the action of 15% sodium hydroxide on cuminaldehyde and methyl nonyl ketone in cold alcoholic solution, and was described as 4-*iso*propylstyryl nonyl ketone, m. p. 144°. We have prepared the compound by a similar method, but find it to be a dimeride, m. p. 150° [Found: C, 84·1; H, 10·7; *M* (Menzies), 605. $C_{42}H_{64}O_2$ requires C, 84·0; H, 10·7%; *M*, 600].

4-Chlorostyryl Nonyl Ketone.—*p*-Chlorobenzaldehyde (2 g.) and methyl nonyl ketone (2·5 g.) were dissolved in alcohol (45 c.c.), and 1 c.c. of 8% sodium hydroxide was added. The product separated after standing for 24 hours at room temperature, and was

recrystallised from alcohol, forming colourless plates, m. p. 62—63° (yield, 2·5 g.) [Found: C, 73·5; H, 8·7; *M* (Menzies), 294. $C_{18}H_{25}OCl$ requires C, 73·8; H, 8·5%; *M*, 293].

Bis-(4-chlorostyryl Nonyl Ketone).—*p*-Chlorobenzaldehyde (2 g.) and methyl nonyl ketone (2·5 g.) were refluxed for 4 hours with 1% alcoholic potassium hydroxide (40 c.c.). The separated product was recrystallised from alcohol, colourless, fine needles being obtained, m. p. 126—127° [Found: C, 73·7; H, 8·3; *M* (Menzies), 614. $C_{36}H_{50}O_2Cl_2$ requires C, 73·8; H, 8·5%; *M*, 585].

3-Chlorostyryl Nonyl Ketone.—This compound was prepared by a method similar to that employed for the 4-chloro-derivative. The product obtained by cooling in ice gave colourless plates on recrystallisation from methyl alcohol, m. p. 57° (Found: C, 74·0; H, 8·6%).

2-Chlorostyryl Nonyl Ketone Semicarbazone.—*o*-Chlorobenzaldehyde (2 g.) and methyl nonyl ketone (2·5 g.) were treated with 0·25% alcoholic potassium hydroxide (20 c.c.) for 7 days. The crude condensation product could not be induced to solidify, and for identification was converted into its *semicarbazone*, which separated from alcohol in colourless needles, m. p. 123—124° (Found: N, 12·1. $C_{19}H_{28}ON_3Cl$ requires N, 12·0%).

2-Hydroxystyryl Nonyl Ketone.—Salicylaldehyde (5 g.) and methyl nonyl ketone (7 g.) were dissolved in absolute alcohol, and sodium hydroxide (30 c.c. of 30%) was added. After standing at room temperature for 5 days, the dark solution was diluted with water and rendered neutral with carbon dioxide. The crude product separated from methyl alcohol (charcoal) in colourless leaflets, m. p. 79° (yield, 5·5 g.) (Found: C, 78·7; H, 9·4. $C_{18}H_{26}O_2$ requires C, 78·7; H, 9·5%).

THE UNIVERSITY, LIVERPOOL. [*Received, June 6th*, 1928.]

CCCVI.—*Ammonium Polysulphides, Hydrogen Pentasulphide, and the Thiocarbonic Acids.*

By HERBERT MILLS and PERCY LUCOCK ROBINSON.

POLYSULPHIDES of ammonium may be prepared by passing hydrogen sulphide into a suspension of sulphur in aqueous ammonia, and Bloxam (J., 1895, **67**, 2707) claimed to have obtained the tetra-, penta-, hepta-, and nona-sulphides in this way, but Thomas and Riding (J., 1923, **123**, 1726), using alcoholic in place of aqueous solutions, only obtained the di-, penta-, and hepta-sulphides. We have prepared the pentasulphide, and bring forward evidence that the alleged heptasulphide is a solid solution of sulphur in the penta-

ılphide, but we have been unable to confirm the existence of the isulphide.

Previous workers (for references see Walton and Parsons, *J. Amer. hem. Soc.*, 1921, **43**, 2539) obtained yellow oils, which on fractional istillation yielded hydrogen disulphide and trisulphide, by treating old concentrated hydrochloric acid with a cold solution of sodium olysulphides. Examination of the solubility of sulphur in hydrogen isulphide led to the inference that the hexasulphide existed below -1·45° (Walton and Whitford, *ibid.*, 1923, **45**, 601). In the present ıvestigation pure anhydrous ammonium pentasulphide has been ecomposed by anhydrous formic acid with the formation of *ydrogen pentasulphide*, the properties of which have been investig- ted.

Red crystals obtained by refluxing ammonium pentasulphide with ırbon disulphide in the manner of Thomas and Riding (*loc. cit.*), and elieved by them to have been $(NH_4)_2S_2$ although analysing to $(NH_4)_2S_{2\cdot2}$, have been shown to be pure ammonium thiocarbonate, $(NH_4)_2CS_3$, whilst a yellow residue, not mentioned by these authors, onsists of ammonium perthiocarbonate, $(NH_4)_2CS_4$. From these lts the corresponding *thiocarbonic acids* have been prepared and ıeir properties investigated.

EXPERIMENTAL.

Ammonium Polysulphides.

Ammonium Pentasulphide.—Sulphur (40 g.) suspended in)0 c.c. of aqueous ammonia (*d* 0·88) and saturated with hydrogen ılphide in the absence of air, gave a deep red solution from which ellow crystals separated slowly on cooling [Found, mean of five osely-agreeing analyses of separate preparations: NH_3, 17·2; $_2S$, 17·1; S, 65·3. Calc. for $(NH_4)_2S_5$: NH_3, 17·4; H_2S, 17·4; 65·2%]; these had all the properties previously ascribed to nmonium pentasulphide.

Ammonium Heptasulphide (alleged).—When greater proportions sulphur were used, the hard cake formed on crystallising was ɔviously non-homogeneous, consisting mainly of yellow penta- lphide together with darker crystals. Hand-picked (*a*) dark red ıd (*b*) orange-red crystals were repeatedly analysed (Table I) and owed both considerable variation amongst themselves and an crease in the sulphur content with darkening colour. Any of these ystals when extracted with cold carbon disulphide gave a yellow ıbstance having all the properties of the pentasulphide. Such ystals are decomposed by water with liberation of sulphur, and hen treated with anhydrous formic acid give a considerable deposit

TABLE I.

Analyses of $(NH_4)_2S_n$.

	NH_3.		H_2S.		S_{n-1}.	
Type of crystal.	Range.	Mean.	Range.	Mean.	Range.	Mean.
Deep red *	10·5—14·3	12·6	11·3—11·8	11·6	70·0—74·0	73·0
Orange red *	14·8—15·2	14·9	14·6—15·0	14·8	68·0—68·3	68·2
$(NH_4)_2S_7$ requires		13·1		13·1		73·8
$(NH_4)_2S_6$ requires		14·9		14·9		70·2

* Number of analyses, four.

of sulphur together with a yellow oil, similar in most respects to that obtained from the pentasulphide. The conclusion reached is that materials of greater sulphur content than the pentasulphide consist of solid solutions of these two substances, and this is borne out by the preparative methods employed by other investigators, *viz.*, (i) allowing saturated alcoholic solutions of pentasulphide to stand in contact with sulphur for 4 months in stoppered bottles, and (ii) slow decomposition of the pentasulphide.

Ammonium Disulphide (alleged).—The preparation of this substance would be of considerable importance, because its decomposition by anhydrous formic acid would probably yield hydrogen disulphide directly. Weighed quantities of ammonium pentasulphide were decomposed in evacuated Faraday tubes, one limb being heated to 100° and the other cooled to −7°, for a considerable period. A yellow liquid, which subsequently solidified to a white solid, collected in the cooled limb and proved on analysis to be ammonium monosulphide [Found: NH_3, 50·1; H_2S, 49·9. Calc. for $(NH_4)_2S$: NH_3, 50·0; H_2S, 50·0%]. The residue of sulphur left in the heated limb amounted to 66·0% of the pentasulphide taken, thus indicating the decomposition $(NH_4)_2S_5 \longrightarrow (NH_4)_2S + 4S$: we have been unable to confirm the observations of Thomas and Riding (*loc. cit.*), who claim that the reaction is represented by $(NH_4)_2S_5 \longrightarrow (NH_4)_2S_2 + 3S$. The fact that the pale yellow liquid or the white solid plunged into either dilute or concentrated hydrochloric acid gives neither free sulphur nor any oil confirms the conclusion indicated by the quantitative synthesis from pentasulphide and the analysis of the material. Thus the decomposition here follows the usual course observed on dry distillation in open vessels or on refluxing with organic solvents, in both of which monosulphide is produced.

Hydrogen Pentasulphide.

The production of hydrogen polysulphides by the wet methods previously employed is invariably accompanied by the precipitation of much sulphur. It has been found that dry ammonium poly-

sulphide crystals give hydrogen polysulphides on treatment with concentrated mineral acids (except nitric) at either laboratory or higher temperatures, but sulphur, varying in extent with the excess of sulphur in the crystals over that required for pentasulphide, is always liberated. Even selected pure pentasulphide yields sulphur under these conditions. Formic acid as concentrated as 90% offers no advantage over mineral acids, but commercial anhydrous formic acid, further dried by phosphorus pentoxide, gives excellent results, the formation of the polysulphide being unaccompanied by free sulphur. Probably the presence of water accounts for the formation of the free sulphur in these reactions.

From ammonium pentasulphide crystals, pale yellow oils were repeatedly prepared in this way and analysed; from Table II it will be seen that the persulphide sulphur (S_{n-1} in H_2S_n) falls only twice below the 82·5% required for H_2S_6, but rises as high as 92·6% (Calc. for H_2S_7 85·0; for H_2S_8 86·8; for H_2S_9 88·3%). Observation proved that the more free sulphur liberated in a reaction the higher was the indicated persulphide sulphur of the accompanying oil. It was believed that the differences found in the oils prepared with

TABLE II.

Acid used.	Persulphide sulphur in separately prepared samples, %.
Hot HCl	92·6, 92·0, 90·3, 90·0, 89·3.
Cold HCl	88·0, 85·0.
Cold anhydrous $H{\cdot}CO_2H$	86·4, 86·1, 85·9, 85·4, 84·9, 84·6, 83·3, 82·3, 81·9.

formic acid were due to differences in the sulphur content of the crystals, and in order to test this, they were ground to a powder and extracted with boiling carbon disulphide. The centrifuged residue gave a reddish-brown oil which had 77% of persulphide sulphur, the low sulphur content and the colour being due to the formation of a certain amount of ammonium perthiocarbonate (see below). If the crystals were extracted with cold carbon disulphide for a short period and centrifuged, the trouble was avoided, and they gave a pale orange-yellow oil, separate specimens of which had persulphide sulphur 79·0, 79·0, 79·3, 79·9, 79·6% respectively, mean 79·3% (H_2S_5 requires 79·0%). The faint orange tint is doubtless due to traces of thiocarbonic acids, and attempts were made to avoid this by extracting the crystals with benzene at various temperatures, but this did not furnish material suitable for the preparation.

Pure *hydrogen pentasulphide* is a thin, clear, yellow oil, which on cooling becomes suddenly viscous at −25°, almost solid at −35°, and glassy at −50°, melting to a clear liquid again on warming; *d* 1·67 at 16° (Found: *M*, cryoscopic in benzene, 152·5. H_2S_5 requires

M, 162). It froths badly at 40°/15 mm., but cannot be distilled. The *solubility of sulphur in the liquid*, *expressed for convenience as* the percentage of sulphur not evolved as hydrogen sulphide, has been found to be 93 at 15°, 90 at 0°, and 88 at −18°. From Walton and Whitford's figures (*loc. cit.*) for the solubility of sulphur in hydrogen trisulphide, similarly expressed, *viz.*, 86·8 at 17·9°, 83·0 at 0·0°, and 71·2 at 15·4°, it is seen to be improbable that the material here considered is a solution of sulphur in a lower sulphide.

Ammonium Thiocarbonates and the Thiocarbonic Acids.

Ammonium thiocarbonates have been described by Yeoman (J., 1921, **119**, 38) and by O'Donoghue and Kahn (J., 1906, **89**, 1812), but they have not been prepared by the methods here used (compare Thomas and Riding, *loc. cit.*).

Ammonium Thiocarbonate.—This is most conveniently obtained by digesting ammonium pentasulphide with carbon disulphide in a wide-necked flask fitted with a cork carrying a wide tube, in which cold water is rapidly circulated, and a reflux condenser. A deposit of white, crystalline ammonium monosulphide first forms on the cold surface, and this is later converted into the pale orange-yellow thiocarbonate by the carbon disulphide vapour. On exposure to moisture or air these orange-yellow crystals turn red. The material obtained from this sublimation process is remarkably pure if washed with carbon disulphide and ether, and centrifuged [Found: NH_3, 23·68; H_2S, 23·40; total S, 65·70. Calc. for $(NH_4)_2CS_3$: NH_3, 23·61; H_2S, 23·61; total S, 66·66%].

Ammonium Perthiocarbonate, $(NH_4)_2CS_4$.—The yellow, crystalline residue from the incomplete refluxing of ammonium pentasulphide in carbon disulphide was shown to be ammonium perthiocarbonate. A better product was obtained by extracting the pentasulphide with carbon disulphide in a Soxhlet apparatus, washing with hot fresh carbon disulphide followed by ether, and then centrifuging [Found: NH_3, 19·10; H_2S, 19·10; total S, 73·88; persulphide S, 19·8. $(NH_4)_2CS_4$ requires NH_3, 19·32; H_2S, 19·32; total S, 72·73; persulphide S, 18·18%].

Earlier workers have been unable to decide satisfactorily whether the acid obtained from thiocarbonates is tri- or tetra-thiocarbonic. Yeoman (*loc. cit.*) considers it to be tetra-, whilst O'Donoghue and Kahn (*loc. cit.*), although believing it to be tri-thiocarbonic, were unable to demonstrate this with certainty.

Trithiocarbonic Acid.—This was prepared by dropping pure solid ammonium thiocarbonate into a large excess of concentrated hydrochloric acid, and the bright red liquid which separated was dried with phosphorus pentoxide [Found: Total S (by Carius), 87·28 (mean

of 8 concordant determinations on independent specimens); *M*, cryoscopic in bromoform, 107·2. H_2CS_3 requires total S, 87·28%; *M*, 110]. The liquid has $d_{4^\circ}^{17\cdot0^\circ}$ 1·47 and freezes sharply to an orange-yellow solid at −30·5°. The surface tension by capillary rise = 48·3 dynes/cm. at 12·5°, giving a parachor of 197·3 (H_2CS_3 requires 201·1, if the parachor of sulphur is taken as 46·2, the mean from the data for carbon disulphide).

The acid decomposes on standing, rapidly at first but more slowly later, evidently forming a red solution of itself in the carbon disulphide produced; distillation of the fresh material leads to its dissociation to carbon disulphide and hydrogen sulphide without residue of sulphur. It is slightly soluble in water, organic solvents, or acids, giving yellow solutions which rapidly decompose with loss of colour. Its behaviour with acetone, in which it dissolves without liberation of sulphur even on long standing, deserves special note because of the marked difference shown by the tetrathiocarbonic acid with this reagent.

Yeoman (*loc. cit.*) has stated that aqueous solutions of pure thiocarbonates do not give the red liquid when acted upon by concentrated hydrochloric acid in the complete absence of oxygen. This statement has been examined by conducting the reaction with the ammonium salt at −5° both in a vacuum and in an atmosphere of hydrogen sulphide, and, provided the concentration of the thiocarbonate is more than sufficient to saturate the hydrochloric acid with thiocarbonic acid, the red liquid separates.

Tetrathiocarbonic (*Perthiocarbonic*) *Acid*, H_2CS_4.—This is a dark brown liquid obtained by the action of 98% formic acid upon ammonium perthiocarbonate, but the total and persulphide sulphur and the estimated molecular weight show considerable variation from sample to sample. The following properties, however, indicate that the liquid is largely composed of this acid. It is decomposed vigorously, with *crackling*, by acetone, giving a colourless solution with deposition of sulphur ($H_2CS_4 \longrightarrow CS_2 + H_2S_2 \longrightarrow H_2S + S$); on distillation under reduced pressure with a small head-column two fractions are obtained—first carbon disulphide, and subsequently a small quantity of a pale yellow oil distilling at 70° and having all the properties of hydrogen disulphide. A large residue of sulphur is left.

It is interesting that concentrated hydrochloric acid used in place of formic acid gives a red liquid which proves to be a solution of sulphur in trithiocarbonic acid. This liquid is soluble in acetone to a yellow solution, without the violence or crackling associated with the hydrogen polysulphides; from this solution the sulphur previously dissolved in the trithiocarbonic acid is slowly precipitated.

On distillation this liquid gives no evidence of a polysulphide, the distillate being colourless carbon disulphide, and the residue sulphur.

It has been observed that ammonium polysulphides and thiocarbonates are only very slowly decomposed by anhydrous formic acid below −7°.

The authors wish to thank Mr. Herbert Smith for assistance in the preparative work, and Electrolux Ltd. for the loan of a refrigerating unit which, after having been fitted with a suitable brine tank, has been in almost constant use during the course of this investigation.

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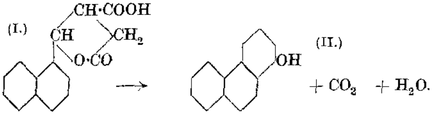
CCCVII.—*The Synthesis of 1-Phenanthrol.*

By JOHN BALDWIN SHOESMITH and ALEXANDER GUTHRIE.

1-PHENANTHROL (II) is the only one of the five theoretically possible monohydroxy-derivatives of phenanthrene not described in the literature. It has been obtained by heating *α-naphthylparaconic acid* (I), loss of carbon dioxide and ring closure with elimination of water taking place as follows :

(I.)



(II.)

α-Naphthaldehyde was prepared (*a*) in a yield of 33% by the catalytic reduction of α-naphthoyl chloride, m. p. 22°, b. p. 158°/12 mm., by Rosenmund's method (*Ber.*, 1918, **51**, 591)—it is noteworthy that in absence of solvent during this reduction the side chain was completely removed and naphthalene produced in quantity—and (*b*) in a yield of 25% by the action of ethyl orthoformate in ethereal solution on magnesium naphthyl bromide in the usual manner. The second is the more convenient method although the yield is somewhat smaller. By both methods the aldehyde was obtained as an oil, b. p. 173—174°/35 mm.; p-*nitrophenylhydrazone*, scarlet needles from acetic acid, m. p. 233—235°.

α-Naphthylparaconic Acid.—α-Naphthaldehyde (7·5 g.), succinic anhydride (5 g.), and anhydrous sodium acetate (6 g.) were heated together under reflux for 6 hours at 122° (a higher temperature causes formation of tarry by-products which render the subsequent purification of the acid difficult); excess of α-naphthaldehyde was

removed from the reaction product in a current of steam, and the residue filtered hot, cooled, extracted with ether, and acidified. The precipitated *α-naphthylparaconic acid* (2 g.) was recrystallised from aqueous alcohol (water 2 parts, alcohol 1 part), from which it separated in well-defined, white, rectangular prisms, m. p. 169° (evolution of carbon dioxide) (Found: C, 70·2; H, 4·7. $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7%).

1-Phenanthrol.—α-Naphthylparaconic acid was heated in a distillation flask immersed in a metal-bath at 180—200° until evolution of carbon dioxide had ceased (30 minutes). The temperature of the bath was then rapidly raised to about 340° and distillation of the vapour prevented by impinging a blast of cold air on the neck of the flask. After 15—20 minutes the temperature was raised again and distillation allowed to proceed. The red oil which distilled over solidified and was dissolved in ether; the ethereal solution was extracted with sodium carbonate to remove carboxylic acids and then with aqueous sodium hydroxide. The latter extract was saturated with carbon dioxide, the precipitate extracted with ether, and the ether evaporated; the *1-phenanthrol* so obtained was crystallised from light petroleum, separating as colourless, prismatic needles, m. p. 156° (Found: C, 85·9; H, 5·2. $C_{14}H_{10}O$ requires C, 86·6; H, 5·2%); yield, 5%. In another experiment crude α-naphthylparaconic acid was used, and the yield of 1-phenanthrol increased to about 15%; this observation is similar to that of Fittig and Erdmann (*Annalen*, 1885, **227**, 242), who found that crude phenylparaconic acid gives a better yield of α-naphthol than does the pure acid.

1-Phenanthrol is stable in air and in solution (contrast the 9-isomeride, which is very unstable, Japp and Findlay, J., 1897, **71**, 1115). It resembles α-naphthol in giving a deep blue coloration on warming with chloroform in alkaline solution, but differs in giving no coloration with glucose solution and concentrated sulphuric acid (compare Molisch's test for carbohydrates). It dissolves in concentrated sulphuric acid with a yellow colour, the solution slowly becoming red and finally colourless when heated. Its alkaline solution gives dyes with diazotised aniline, etc. The picrate crystallises in orange-red, feathery needles, m. p. 182°, from methyl alcohol.

In order to characterise the compound further it was methylated as follows. To 1-phenanthrol (0·8 g.) dissolved in 8 c.c. of methyl alcohol, 4 c.c. of 10% methyl-alcoholic potassium hydroxide and 8 c.c. of a 13% solution of methyl sulphate in methyl alcohol were added, and the solution was heated on the steam-bath for 1 hour, after which it was diluted with water, extracted with ether, the

ethereal solution extracted with alkali to remove unchanged phenanthrol, and the 1-methoxyphenanthrene left on evaporation was recrystallised from methyl alcohol; yield, 50%. The colourless prismatic needles had m. p. 105°, and were found to be identical in all respects with a sample of 1-methoxyphenanthrene prepared by the method described by Pschorr, Wolfes, and Buckow (*Ber.*, 1900, **33**, 170).

The authors wish to acknowledge the grant of a Carnegie Teaching Fellowship to one of them (J. B. S.) during the tenure of which the investigation was carried out.

EDINBURGH UNIVERSITY. [*Received, June 28th*, 1928.]

CCCVIII.—*Alternating Reactive Positions in the Nucleus of* tert.*-Butylbenzene.*

By JOHN BALDWIN SHOESMITH and ALEXANDER MACKIE.

IT is well known that when a substituent enters the nucleus of *tert.*-butylbenzene it does so almost exclusively in the para-position, *i.e.*, as far as possible from the *tert.*-butyl group. The isolation of ortho-compounds has been reported in only two cases: Seńkowski (*Ber.*, 1890, **23**, 2414), claimed to have prepared both ortho- and para-nitro-*tert.*-butylbenzenes by direct nitration, and Kozak (*Bull. Akad. Sci. Cracow*, 1906, 407) brominated the hydrocarbon and submitted the reaction product to the action of methyl iodide and sodium, whereby he isolated two isomeric *tert.*-butyltoluenes, one of which he described as the ortho-compound. Since Malherbe (*Ber.*, 1919, **52**, 319) was unable to repeat Seńkowski's results, the evidence that reaction can take place at both ortho- and para-positions is confined to the observations of Kozak.

It has now been proved that Seńkowski isolated *o*-nitro-*tert.*-butylbenzene, and a further example has been obtained of the alternating influence of the *tert.*-butyl group in that, when treated with hydrogen iodide, the isomeric iodo-*tert.*-butylbenzenes only react if the iodine is in the *o*- or *p*-position.

o-*Nitro-*tert.*-butylbenzene.*—It was not found possible to prepare this compound by direct nitration (compare Malherbe, *loc. cit.*), but it was obtained in the following manner. *p*-Nitro-*tert.*-butylbenzene (the constitution of which was proved definitely by Malherbe) on further nitration gives a dinitro-compound, m. p. 62°, which might be 2 : 4- or 3 : 4-dinitro-*tert.*-butylbenzene, the latter possibility requiring consideration because of the inhibiting effect of the *tert.*-butyl group on substitution in the ortho-position. The

dinitro-compound on reduction with ammonium hydrogen sulphide gives a nitroamino-compound, m. p. 55°, and elimination of the amino-group gives an oil, b. p. 250·5°/765 mm.; this can be converted into an amine of which the acetyl derivative has m. p. 161° and strongly depresses the m. p. of *p*-acetamido-*tert.*-butylbenzene (169°). Since the m. p. of the corresponding meta-compound, which would result in the same way from the 3 . 4-isomeride, is 99° (see p. 2338), this leaves no doubt as to the constitution of the *o*-nitro-compound and also classifies the nitroamino-compound as *2-nitro-4-amino-*tert.*-butylbenzene*, and the dinitro-compound as 2 : 4-dinitro-*tert.*-butylbenzene. The above proof is necessitated by the fact that it was not found possible to obtain *o*-nitrobenzoic acid from *o*-nitro-*tert.*-butylbenzene, a point stressed by Seńkowski (*loc. cit.*), who gave the b. p. of the compound as 247—248°/738 mm. and the m. p. of the *o*-acetamido-compound as 159°.

*The Reduction of the Isomeric Iodo-*tert.*-butylbenzenes.*—The ease of removal of iodine from these compounds by hydrogen iodide is $o > p > m$, and the comparative ease with which the ortho-isomeride was reduced shows that iodine may be removed from a position which is almost immune from attack by the ordinary substituting reagents. This can readily be understood if the preliminary stage in the replacement of iodine by hydrogen is the attraction of a proton to a negatively polarised position such as would be expected to occur in both the ortho- and para-positions in the nucleus of *tert.*-butylbenzene. It would not be expected that the attachment of a proton in the ortho-position would be inhibited to the same extent as that of the more bulky molecules of nitrating, halogenating, and sulphonating agents; moreover, when these experiments are compared with the corresponding experiments in the toluene series (Shoesmith and Slater, J., 1924, **125**, 2278), it is found that whilst the rates of removal of iodine from *o*-iodotoluene and *o*-iodo-*tert.*-butylbenzene are similar, the quantities of ortho-compounds formed by direct substitution of the corresponding hydrocarbons are markedly different.

The Behaviour of o-*Bromo-*tert.*-butylbenzene with Magnesium.*—In a recent communication, Tschitschibabin, Elgasine, and Lengold (*Bull. Soc. chim.*, 1928, **43**, 238) have stated that when the mixture produced by the bromination of *tert.*-butylbenzene is allowed to react with magnesium, followed by ethyl orthoformate, *p-tert.*-butylbenzaldehyde is formed exclusively, since on oxidation only *p-tert.*-butylbenzoic acid could be isolated. They conclude that any *o*-bromo-*tert.*-butylbenzene present does not form a magnesium derivative. As the present authors had already found that *o-iodo-*

tert.-*butylbenzene* readily gives a Grignard reagent, this appeared remarkable, and o-*bromo*-tert.-*butylbenzene* was therefore prepared as follows : *p*-Nitro-*tert.*-butylbenzene is brominated with difficulty at 90° in presence of finely divided iron, giving a compound which must be 2-*bromo*-4-*nitro*-tert.-*butylbenzene*, since on reduction it gives an amine the *acetyl* derivative of which is different from 3-bromo-4-acetamido-*tert.*-butylbenzene (the only other possible reaction product). 2-*Bromo*-4-*amino*-tert.-*butylbenzene* on elimination of the amino-group gives *o*-bromo-*tert.*-butylbenzene which in ethereal solution reacts *vigorously* with magnesium, and from the product o-tert.-*butylbenzoic acid* may be produced in the usual manner. This acid may also be prepared from the *o*-iodo-derivative. The authors do not suggest that this is additional evidence in favour of the polarisation of the ortho-position, but merely wish to point out that the steric effect of the *tert.*-butyl group is not sufficient to inhibit a reaction involving the attack by magnesium of a halogenated ortho-position.

EXPERIMENTAL.

There is much confusion in the literature with respect to *iso*- and *tert.*-butylbenzene derivatives, and we therefore used as our starting product the authentic *tert.*-butylbenzene prepared by the method of Schramm (*Monatsh.*, 1888, **9**, 615), who proved that *iso*- or *tert.*-butyl chloride condensed with benzene in presence of aluminium chloride to give *tert.*- and not *iso*-butylbenzene. References which describe compounds as *iso*butyl when in reality they are *tert.*-butyl are marked with an asterisk.

*iso*Butyl alcohol was converted to a mixture of *iso*- and *tert.*-butyl chlorides by means of zinc chloride and phosphorus trichloride (Dehn and Davis, *J. Amer. Chem. Soc.*, 1907, **29**, 1332), but only a 32% yield could be obtained, the chief product being apparently a mixture of polymerised butylenes. The mixed chlorides were condensed with benzene as described by Schramm (*loc. cit.*); continuous stirring and efficient condensing apparatus improved the yield (27%), and *white* aluminium chloride of very good quality was found to be advantageous. The *tert.*-butylbenzene had b. p. 165—170°.

p-*Nitro*-tert.-*butylbenzene*.—Nitric acid (*d* 1·52) was gradually added to an equal weight of vigorously stirred *tert.*-butylbenzene at the ordinary temperature ; when reaction was complete (2 hours), the mixture was poured into water, and the yellow oil washed with water, dried, and distilled : b. p. 125—130°/10 mm. It could not be solidified.

2 : 4-*Dinitro*-tert.-*butylbenzene*.—A mixture of nitric acid (*d* 1·51 ; 2 parts by weight) and concentrated sulphuric acid (3 parts) was

added during 5 hours to vigorously stirred *tert.*-butylbenzene (1 part) maintained at 60°. The nitration product was poured on ice, and the precipitated yellow oil slowly solidified. The solid was filtered off and washed with water. It crystallised from aqueous alcohol in white prisms, m. p. 61—62° (compare Malherbe, *loc. cit.*, and Baur, *Ber.*, 1894, **27**, 1610), which slowly turned yellow on exposure to light. The same compound was obtained by heating vigorously stirred *p*-nitro-*tert.*-butylbenzene with an equal weight of nitric acid (*d* 1·51) at 60° for 2—4 hours.

2-*Nitro*-4-*amino*-tert.-*butylbenzene*.—Finely divided 2 : 4-dinitro-*tert.*-butylbenzene (20 g.) was added to a mixture of ethyl alcohol (76 c.c.) and ammonia (*d* 0·880; 10 c.c.), and hydrogen sulphide passed into the mixture for one hour, the reaction flask being occasionally agitated. The mixture was then heated for a few minutes on the steam-bath, cooled, and the process repeated. To the reaction mixture an excess of water was added, and the nitro-amino-compound, precipitated as a yellow solid mixed with sulphur, was filtered, washed with water, and heated under reflux with an excess of hydrochloric acid (*d* 1·05) for 5 minutes. The solution was filtered from sulphur, the filtrate cooled until the hydrochloride commenced to crystallise out, and an excess of ammonia (*d* 0·880) was immediately added. The nitroamine separated as an oil which rapidly solidified; yield 71%. 2-*Nitro*-4-*amino*-tert.-*butylbenzene* crystallises from aqueous alcohol as yellow plates, and from light petroleum as yellow needles, m. p. 55° (Found: N 14·7. $C_{10}H_{14}O_2N_2$ requires N, 14·4%). When boiled with acetic anhydride, it gives the acetyl derivative, colourless needles, m. p. 112° from aqueous alcohol.

o-*Nitro*-tert.-*butylbenzene*.—To the amino-compound (1 part), dissolved in absolute alcohol (3 parts), concentrated sulphuric acid (3 parts) was added, and the whole cooled to 0°; the sulphate crystallised out and the amine was diazotised, the reaction mixture then being allowed slowly to attain the laboratory temperature and finally heated on the steam-bath. *o*-Nitro-*tert.*-butylbenzene was removed in a current of steam, extracted from the distillate with ether, and ultimately obtained as a yellow oil (yield 54%) with a characteristic odour, b. p. 114—115°/10 mm. or 250·5°/765 mm.

o-*Amino*-tert.-*butylbenzene*.—Fine iron filings (12 g.) were mixed with water (15 c.c.) and the mixture slowly stirred and heated whilst 1 c.c. of glacial acetic acid and 0·3 c.c. of *o*-nitro-*tert.*-butylbenzene were added; the temperature was raised to 90° and 10 g. of the *o*-nitro-compound were slowly introduced during 3 hours. After a further 2 hours' heating, the amine was distilled in steam, extracted from the distillate with ether, dissolved in dilute hydrochloric acid,

4 H

separated from unchanged nitro-compound by ether extraction, and precipitated from its hydrochloric acid solution by addition of ammonia; when re-extracted with ether and purified by distillation it had b. p. 102°/10 mm.; yield 75%. The amine was found to be a colourless liquid, very volatile in steam, becoming red on exposure to air which caused separation of a small quantity of crystals, probably carbonate (compare Seńkowski, *loc. cit.*). *o*-Acetamido-*tert.*-butylbenzene was obtained from the amine in the usual way, and crystallised from benzene in prismatic needles, m. p. 161° (Seńkowski gives 159°).

*o-Iodo-*tert.*-butylbenzene.*—Dilute sulphuric acid (60 c.c.; *d* 1·12) was added to the above amino-compound (5·5 g.), the whole well stirred to ensure formation of a finely divided precipitate of amine sulphate, and the latter diazotised by a solution of sodium nitrite (5 g. in 10 c.c. of water) at −10°. The diazonium sulphate is very unstable and appeared to decompose at about −8°. Potassium iodide (15 g.) in water (25 c.c.) was then rapidly added to the *very vigorously stirred* diazo-solution, the temperature was allowed slowly to rise to 18°, and decomposition completed on the steam-bath. Excess of aqueous alkali was added to the reaction mixture to remove free iodine, and the iodo-compound distilled in a current of steam. The ethereal extract of the distillate finally yielded an oil, and that from several experiments was fractionated under reduced pressure. o-*Iodo*-tert.-*butylbenzene* is a colourless oil, b. p. 116—118°/10 mm. (Found: I, 48·3. $C_{10}H_{13}I$ requires I, 48·8%); yield 13%.

m-*Iodo*-tert.-*butylbenzene.*—This was obtained as follows: *p*-nitro-*tert.*-butylbenzene was reduced by iron and hydrochloric acid (as for the ortho-compound), the amino-derivative acetylated (m. p. of acetamido-compound, 169°; Malherbe, *loc. cit.* gives 169°), the acetyl derivative nitrated at 35—40° by acid of *d* 1·46, and the product hydrolysed by alkali to *m*-nitro-*p*-amino-*tert.*-butylbenzene; the amino-group was removed and the resulting nitro-compound reduced (as before) to *m*-amino-*tert.*-butylbenzene (an oil of b. p. 107—108°/9 mm.); acetylation then gave a product of m. p. 99° (Gelzer, *Ber.*, 1888, **21**, 2949 gives 101°) from which the amino-compound was regenerated, and this was finally converted into the iodo-compound. m-*Iodo*-tert.-*butylbenzene* is a liquid, b. p. 106—108°/9 mm. (Found: I, 48·4. $C_{10}H_{13}I$ requires I, 48·8%).

p-Iodo-*tert.*-butylbenzene, obtained by the usual methods from the *p*-nitro-compound, distilled at 116—118°/9 mm. (compare Willgerodt and Rampacker, *Ber.*, 1901, **34**, 3669; Pahl,* *Ber.*, 188[?], **17**, 1233; Boedtker, *Bull. Soc. chim.*, 1906, **35**, 832). It is noteworthy that whilst *o*-*tert.*-butylbenzenediazonium sulphate is ve

* See p. 2336.

unstable even at 0°, the *m*- and *p*-isomerides are comparatively stable, a phenomenon which is paralleled in the corresponding toluene derivatives.

o-*Bromo*-tert.-*butylbenzene*. — 2 - *Bromo*-4 - *nitro*-tert.-*butylbenzene* was prepared by heating *p*-nitro-*tert*.-butylbenzene (6 g.) with bromine (7 g.) in presence of finely divided iron (1·2 g.) in a flask fitted with a reflux condenser and calcium chloride tube, to about 90°. Evolution of hydrogen bromide was moderately brisk, and after about ½ hour, a further 7 g. of bromine were slowly added and the whole was heated for 7 hours. When cold, the product formed a semi-solid mass, and on distillation in a current of superheated steam, a yellow, oily solid slowly collected in the receiver. This was filtered off, pressed on a porous plate, and crystallised from alcohol, forming long, colourless needles, m. p. 94·5° (Found: Br, 30·6. $C_{10}H_{12}O_2NBr$ requires Br, 31·0%). This bromination is much slower than that of *p*-nitrotoluene, but if all unbrominated oil is recovered, a yield of about 88% may be obtained.

2-*Bromo*-4-*amino*-tert.-*butylbenzene*. Concentrated hydrochloric acid (1 c.c.) was added to a solution of the foregoing bromo-compound (7·5 g.) in 30 c.c. of alcohol, and the mixture heated under reflux to the boiling point, finely divided iron (5 g.) then being added in 4 equal portions. After 2 hours, reduction was complete and the alcoholic solution was filtered from iron, water added to the filtrate, and the filtrate extracted with ether. The amine hydrochloride, precipitated on the addition of hydrochloric acid to the ethereal extract, was filtered, washed with ether, and dissolved in hot dilute hydrochloric acid, the amine then being precipitated by addition of concentrated ammonia and extracted with ether. After distillation of the ether, 2-*bromo*-4-*amino*-tert.-*butylbenzene* was obtained as a pale yellow liquid, b. p. 153—155°/11 mm. (Found: Br, 35·1. $C_{10}H_{14}NBr$ requires Br, 35·1%); yield 70%. Its *hydrochloride* has m. p. 235° (decomp.), and its *acetyl* derivative crystallised from aqueous alcohol in colourless rectangular plates, m. p. 142—143°.

o-*Bromo*-tert.-*butylbenzene*. The amino-group was eliminated from 2-bromo-4-amino-*tert*.-butylbenzene as for the corresponding *o*-nitro-compound. The diazonium compound was unstable and decomposed above −2°. o-*Bromo*-tert.-*butylbenzene* is a colourless liquid, b. p. 96—98°/12 mm. (Found: Br, 38·0. $C_{10}H_{13}Br$ requires Br, 37·6%); yield 54%.

o-tert.-*Butylbenzoic Acid*.—*o*-Bromo (or *o*-iodo)-*tert*.-butylbenzene was dissolved in ether and the equivalent quantity of magnesium added. On the addition of a crystal of iodine, reaction commenced immediately and continued at the ordinary temperature until almost

all the magnesium had disappeared. The flask was finally heated on the water-bath for 1 hour, after which a current of carbon dioxide was passed into the solution for approximately 15 hours. The viscous mass was disintegrated by the addition of ice, followed by dilute hydrochloric acid, the whole extracted with ether, the ethereal layer in turn extracted with sodium carbonate solution, which was acidified with dilute acid, and again extracted with ether. *o*-tert.-*Butylbenzoic acid* was thus obtained after crystallisation from aqueous alcohol (20%) as well-defined, hexagonal plates, m. p. 68·5° (Found: C, 73·8; H, 7·8. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·9%); yield 60%.

Reduction of the Isomeric Iodo-tert.-*butylbenzenes.*—A weighed quantity (*w*) of each of these was allowed to stand at 25° in a solution of glacial acetic acid containing 0·40 g. of hydrogen iodide per c.c., and the rate of reduction measured as previously (Shoesmith and Slater, *loc. cit.*). The results are recorded below, *t* being the time in days, and *x* the proportion changed.

	o-Isomeride (*w* = 0·3955 g.).	*p*-Isomeride (*w* = 0·4045 g.).
t.	*x*.	*x*.
2	61%	11%
4	76	19
14	86	35

The meta-isomeride was unaffected under these conditions. The order of reduction was unchanged even at 100° and 110°.

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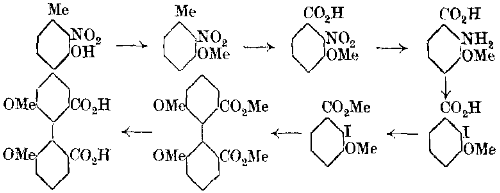
CCCIX.—*The Molecular Configurations of Polynuclear Aromatic Compounds. Part VIII.* 6 : 6′-*Dimethoxydiphenic Acid.*

By JAMES KENNER and HAROLD AUGUSTUS TURNER.

THE relatively simple method of preparing 2-nitro-*m*-cresol devised by Gibson (J., 1923, **123**, 1273; compare Hodgson and Beard, J., 1925, **127**, 498) has rendered it easily accessible and thus provided a convenient starting point for the synthesis of 6 : 6′-*dimethoxy*-

diphenic acid. This has been achieved by the following series of reactions :



The acid was found to be asymmetric, and was conveniently resolved into optically active forms by means of its *quinine* salts, a partial resolution being also achieved by means of quinidine.

EXPERIMENTAL.

2-*Nitro*-m-*cresol*.—The conditions of sulphonation and nitration of *m*-cresol prescribed by Gibson (*loc. cit.*) were followed, but it was found advisable to employ only 50 c.c. of water in place of 100 c.c. for dilution prior to steam distillation, and to conduct this operation at first so that the temperature of the vapour issuing from the distillation flask was 110°. After about 200 c.c. of distillate had been collected, the temperature of distillation was rapidly raised to 130—160°. The buttery mass of 2-nitro-*m*-cresol then obtained was suitable for immediate treatment with methyl sulphate and alkali, but could, if desired, be further purified by freezing. It was unnecessary to distil the crude methyl ether, since it crystallised when stirred or inoculated with the pure material, and could then be purified by crystallisation from dilute alcohol. For its oxidation, the ether (5 g.) was boiled with a solution of potassium permanganate (13 g.) in water (550 c.c.).

2-Amino-3-methoxybenzoic acid (Pschorr, *Annalen*, 1912, **391**, 27) was converted by the ordinary procedure into 2-*iodo*-3-*methoxybenzoic acid*, which crystallised from dilute alcohol in yellowish needles, m. p. 150—151° (Found : *M*, 281. $C_8H_7O_3I$ requires *M*, 279). Its *methyl* ester crystallised from benzene–light petroleum in prisms, m. p. 57°, and was converted by treatment with an equal weight of copper powder at 205—210° into *methyl* 6 : 6′-*dimethoxydiphenate*, which crystallised from benzene in small prisms, m. p. 137—138° (Found : C, 65·01 ; H, 5·78. $C_{18}H_{18}O_6$ requires C, 65·45 ; H, 5·45%). 6 : 6′-*Dimethoxydiphenic acid* was precipitated as a gummy mass from a cold solution of its sodium salt, but in the

crystalline condition from hot solutions; by crystallisation from alcohol, it was obtained in stout prisms, m. p. 288—290° (decomp.) (Found: C, 63·25; H, 4·7; *M*, 153. $C_{16}H_{14}O_6$ requires C, 63·57; H, 4·6%; *M*, 151).

Brucine hydrogen dimethoxydiphenate was obtained as a uniform salt, m. p. 268° (Found: N, 4·4. $C_{39}H_{40}O_{10}N_2$ requires N, 4·0%), and acid to phenolphthalein, when the acid was treated with two molecular proportions of brucine hydrate. Its sparing solubility in acetone rendered it easily separable from the unneutralised brucine, and the salt separated in prisms from a mixture of chloroform and acetone.

Resolution of the Acid into Optically Active Components.—A solution of the acid (3 g.) in methyl alcohol (70 c.c.) was neutralised by a solution of quinine hydrate (7·54 g.) in methyl alcohol (30 c.c.), and the solvent then evaporated. When the residue was triturated with successive amounts of cold acetone (200 c.c. in all), 4·5 g. remained undissolved, whilst a resinous mass (5·3 g.) was recovered from the acetone. In other experiments a similar separation was achieved by means of ethyl acetate.

Quinine l-*dimethoxydiphenate* (Found: N, 5·91. $C_{56}H_{60}O_{10}N_4$ requires N, 5·89%), the less soluble of the two salts thus obtained, melted at 172—173° after crystallisation from acetone, and this m. p. was unaffected by two further crystallisations from the same solvent. It had $[\alpha]_D$ + 126° (c = 0·95 in chloroform; l = 1), and the corresponding ammonium salt, prepared by shaking the quinine salt with chloroform and a slight excess of dilute ammonia, and repeatedly extracting the aqueous solution with chloroform, had $[\alpha]_D$ −291° (c = 0·59 in water; l = 1): the strength of the solution was determined by evaporating an aliquot portion. The free l-*acid* was precipitated from a solution of the sodium salt similarly prepared, and, after being dried in a vacuum at the ordinary temperature to constant weight, had $[\alpha]_D$ −115° (c = 0·56 in acetone; l = 2); it was only sparingly soluble in chloroform or ether, and melted at 294—295°.

When the resin mentioned above was rubbed with successive small quantities of cold ether, it was obtained in the form of a powder which gradually shrank and decomposed about 60°. It was easily soluble in benzene, but was precipitated as an oil by ligroin, and could not be crystallised; when dried to constant weight it had $[\alpha]_D$ −68° (c = 1·27 in chloroform; l = 1) and an aqueous solution of the ammonium salt prepared from it had $[\alpha]_D$ +254°. Clearly, therefore, the resin was a fairly pure sample of *quinine* d-*dimethoxydiphenate*.

A mixture of salts was also obtained when the acid (4·5 g.) was

neutralised by anhydrous quinidine (9·75 g.) in methyl-alcoholic solution. The product was easily soluble in methyl alcohol, acetone, and ethyl acetate, but an incomplete separation was achieved by allowing the solution of the mixed salts in benzene (50 c.c.) and ligroin (300 c.c.; b. p. 90—110°) spontaneously to evaporate. The weights, melting points, and specific rotatory powers in 2% alcoholic solution of the five successive fractions of prismatic crystals obtained were 1·8 g., m. p. 171—174°, $[\alpha]_D$ +88° (Found: N, 5·5%); 3·3 g., 170—176°, −23°; 1·0 g., 169—175°, −20°; 1·5 g., 170—175°, +50°; 1·7 g., 173—179°, +76° (Found: N, 5·8. $C_{56}H_{60}O_8N_4$ requires N, 5·9%). For a 0·4% solution of the sodium salt prepared from the first fraction, $[\alpha]_D$ −216°, whilst the second fraction yielded a totally inactive solution.

THE UNIVERSITIES OF
SHEFFIELD AND SYDNEY. [*Received, July 7th, 1928.*]

CCCX.—*The Chemistry of the Three-carbon System. Part XVIII. Quantitative Investigations on the Influence of Alkyl Substituents on the αβ–βγ Change in Unsaturated Acids: Observations on the Reduction of Sorbic Acid, and a New Synthesis of Pyroterebic Acid.*

By ALAN AUGUST GOLDBERG and REGINALD PATRICK LINSTEAD.

THE position of equilibrium in the reversible change between αβ- and βγ-olefinic acids in the presence of alkali appears to be independent of the physical conditions under which the interconversion proceeds (Linstead, J., 1927, 362, 2579). It has, therefore, become possible to ascertain the effect of internal conditions, *i.e.*, molecular substitution, upon the position of equilibrium and upon the ease with which it is attained. The present communication describes an examination of the simplest mono-olefinic acids from this point of view.

In the two butenoic acids, *viz.*, vinylacetic (βγ-) and crotonic (αβ-), the change appears to be irreversible in the direction βγ ⟶ αβ, and the same preponderance of the αβ-form is met with in α- and β-alkylcrotonic acids, although, since in many instances only the αβ-forms have as yet been isolated, the evidence is not final. With

$$\text{(I.)}\ CH_3{\cdot}CR_\gamma{:}CR_\beta{\cdot}CHR_\alpha{\cdot}CO_2H \overset{KOH}{\rightleftharpoons} CH_3{\cdot}CHR_\gamma{\cdot}CR_\beta{:}CR_\alpha{\cdot}CO_2H\ \text{(II.)}$$

the pentenoic acids, a balanced reaction is possible, and we have therefore examined the unsubstituted pentenoic acids themselves

($R_{\alpha,\beta,\gamma} = H$), and two of the three monomethyl derivatives (R_α or $R_\gamma = Me$), the third possible series ($R_\beta = Me$) having already been studied (Kon and Linstead, J., 1925, **127**, 618; Linstead, J., 1927, 355). In addition, the effect of lengthening the chain ("δ-substitution," resulting in the *n*-hexenoic acids) was investigated, and the *cyclo*pentenylacetic acids (III and IV) were studied for comparison with the *cyclo*hexenyl analogues. The unsubstituted

$$\text{(III.)}\ \begin{matrix} CH_2{\cdot}CH_2 \\ CH_2{\cdot}CH_2 \end{matrix}\!\!>\!C{\cdot}CH_2{\cdot}CO_2H \overset{KOH}{\rightleftharpoons} \begin{matrix} CH_2{\cdot}CH_2 \\ CH_2{\cdot}CH_2 \end{matrix}\!\!>\!C{:}CH{\cdot}CO_2H\ \text{(IV.)}$$

pentenoic and hexenoic acids were of especial interest as they were among the original substances studied by Fittig (*Annalen*, 1894, **283**, 47).

The preparation of the ten unsaturated acids used in this work is described in the experimental portion. The methods available for the preparation of α-methyl-Δ^α-pentenoic acid (*II*; $R_\alpha = Me$, $R_{\beta,\gamma} = H$) did not appear to be very satisfactory, but we find that it can readily be prepared in a state of purity from propaldehyde through the aldol $CH_3{\cdot}CH_2{\cdot}CH(OH){\cdot}CHMe{\cdot}CHO$, by dehydration and oxidation by the method of Delépine and Bonnet (*Compt. rend.*, 1909, **149**, 39). A detailed investigation was made into the preparation of terebic acid which was required in the synthesis of pyroterebic acid (I; $R_\gamma = Me$, $R_{\alpha,\beta} = H$): the methods involving the oxidation of pinene and camphor appeared to afford uncertain yields and were not examined, but the remaining methods were investigated and much the best was found to be that due to Stobbe, in which teraconic acid is prepared from acetone and succinic ester and subsequently isomerised to terebic acid. We were able to improve upon Fittig's final method for the preparation of pyroterebic acid, but subsequently developed a new method (see pp. 2349, 2354).

Equilibration of the Acids.—In examining the interconversion between the pairs of acids, both the temperature and the concentration and excess of catalyst were maintained at the standard figures used in previous work, and analyses of the mixed acids were again carried out by iodometric methods. In all cases, when the pure isomeric acids were treated with 25% potassium hydroxide at 100°, the same equilibrium was reached in a few hours from either side. In the two pairs of acids already examined by Fittig we were able to confirm and amplify his statement that the equilibrium is on the αβ side, but our results differ in that, using 25% alkali (Fittig used 10 or 20%), we could detect only very slight formation of β-hydroxy-acid—generally about 2%. This absence of pronounced side reaction serves to support the evidence already obtained (J., 1927, 362) as to the tautomeric nature of the change.

The movement towards equilibrium is shown for three of the aliphatic series in Fig. 1 and for the alicyclic acids in Fig. 2, where the results previously obtained for the *cyclo*hexenylacetic acids are added for comparison. The more important data are summarised in Table I, the approximate time (in hours) required for equilibration being given in the last column.

FIG. 1.

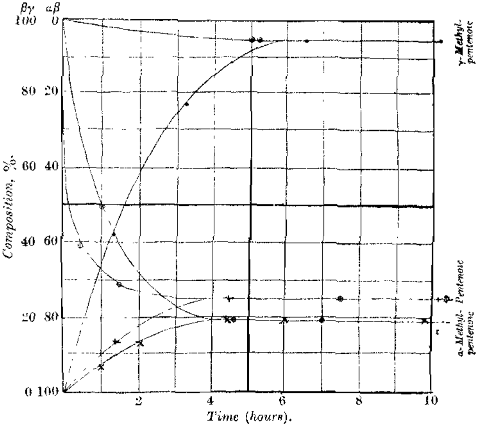


TABLE I.

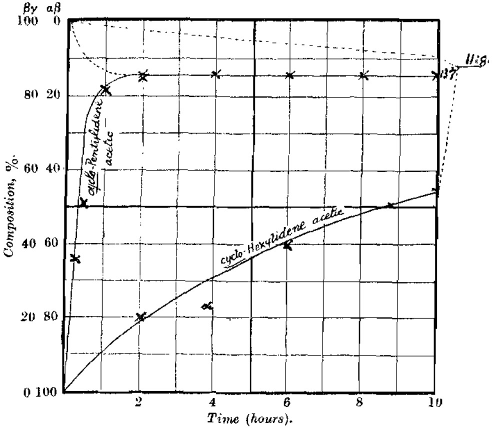
Interconversion under Standard Conditions.

Acid (as αβ form).	% of αβ-acid at equilibrium.			Time.
	From αβ-acid.	From βγ-acid.	Mean.	
Δ^{α}-Pentenoic	75·6, 75·4, 75·2	75·6, 75·4	75·4	3
α-Methyl-Δ^{α}-pentenoic ...	80·9, 80·2, 80·5	81·2, 80·7	80·7	4½
γ-Methyl-Δ^{α}-pentenoic ...	6·0, 5·1, 5·4	5·4, 6·3	5·6	6
*cyclo*Pentylideneacetic ...	{13·7 13·7; 13·7 13·5}	13·7	13·7	2

The Hexenoic Acids.—The results obtained from the hexenoic acids were abnormal and presented several features of interest. The αβ-acid behaved normally: treatment with alkali resulted in a fall in boiling point and an increase in affinity for iodine, indicating

the production of the βγ-isomeride. After some 4 hours the iodine value of the product became constant (% addition of iodine, 19·9), and was unchanged by further treatment; when, however, the βγ-acid (hydrosorbic acid) was treated similarly, a very slow fall in the iodine value of the product was observed, becoming constant after about 20 hours' treatment at an addition value of 47·4%. Even on prolonged treatment with stronger alkali at the boiling point no further change could be effected. Hence, equilibrium

Fig. 2.

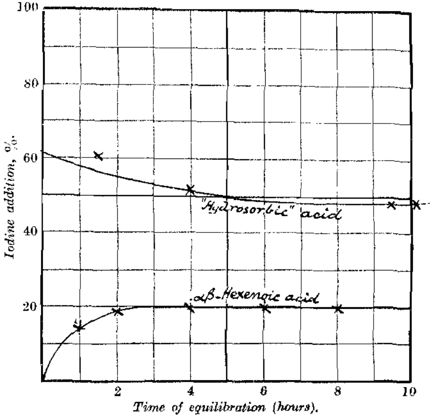


was not attained, as shown in Fig. 3, where the time of reaction is plotted against the iodine addition of the product.

The three possible explanations of these anomalous results were: (1) the use of unsuitable experimental methods, (2) the presence of impurity in the acid used, or (3) definite abnormality of the βγ-acid in its behaviour with caustic alkali. The first explanation was not considered probable on account of the excellent results already obtained with other acids, whilst the third seemed unlikely, since the βγ-acid formed from the αβ-isomeride in equilibration behaved normally. On the other hand, the βγ-acid had been prepared from sorbic acid by the method due to Fittig and Baker (*Annalen*, 1894, **283**, 117) and subsequently used by a number of investigators.

The authenticity of our acid was carefully checked. It had a sharp boiling point, the correct physical properties, and gave the anilide, m. p. 55°, described by von Auwers and Henya (*Annalen*, 1923, **434**, 140). It was noticed, however, that the anilide had an indefinite m. p. even after repeated crystallisation, and that the difference

FIG. 3.



between this and the m. p. of the anilide of the αβ-acid was unusually large, thus :

Series.	Pentenoic.	Hexenoic.	α-Methyl-pentenoic.	γ-Methyl-pentenoic.
M. p. of αβ-anilide......	100°	109—110°	84°	119°
M. p. of βγ-anilide......	75	54—56	75	106
Difference	25	55	9	13

This abnormality suggested the presence of impurity in the βγ-acid, which might be either the αβ- or the γδ-isomeride, formed by 3 : 4- and 1 : 2-addition of hydrogen to sorbic acid, respectively. The iodine addition was high, and therefore the presence of αβ-acid (or of fully reduced acid) was unlikely, and, moreover, acid containing αβ-acid as impurity would give normal results on equilibration. The γδ-acid, on the other hand, appeared to be a probable impurity : its physical properties closely resemble those of the βγ-isomeride (Fichter, *Ber.*, 1896, **29**, 2367), and its presence would account for

the observed abnormalities, for it would be expected to resemble allylacetic acid in its inertness towards alkali. A study of the literature showed that Fittig's work, which established the presence of the $\beta\gamma$-isomeride in his hydrosorbic acid without, we think, proving its homogeneity, had always been accepted without verification. Indeed, in the course of one oxidation (*Annalen*, 1892, **268**, 38) he obtained a small quantity of succinic acid which could only have been derived from the $\gamma\delta$-acid. The bulk of the chemical evidence is ambiguous. We have oxidised samples of hydrosorbic acid prepared from sorbic acid by Fittig's method: with ozone, succinic acid and a mixture of acetaldehyde and propaldehyde were obtained, whilst with alkaline permanganate, succinic, propionic, and acetic acids were all identified. From the proportions of these oxidation products and from the equilibration experiments on the original acid, it is estimated that the "hydrosorbic acid" prepared in this way contained rather more than 50% of the $\gamma\delta$-isomeride. The reduction of sorbic acid was then repeated both with aluminium amalgam (which had little action) and with sodium amalgam under a variety of conditions; we were unable to isolate the pure $\beta\gamma$-acid from any of the products, and indeed in one experiment a mixture containing about 90% of the $\gamma\delta$-acid was obtained, which was hardly affected by prolonged treatment with alkali. No separation of the acids could be effected by fractional crystallisation of the cadmium salts, as suggested by Fichter's work. The *p*-toluidide of our acid formed mixed crystals (well-defined needles, m. p. 74—77°), whereas the m. p. of the pure $\gamma\delta$-derivative is 103° and that of pure hydrosorbic acid (prepared from the corresponding paraconic acid) is 95·5° (Fichter and Pfister, *Ber.*, 1904, **37**, 1997). The preparation and equilibration of hydrosorbic acid will shortly be described, but it may be said that equilibrium is attained in about 4 hours at about 77% of $\alpha\beta$-acid.

Two points of interest arise. (1) It is believed that this represents the first proof of 1 : 2 addition to a conjugated system of this type, although it was predicted by Burton and Ingold (this vol., p. 913); more recently, in the course of their study of the hydrogenation of conjugated systems, Farmer and his collaborators have obtained other examples of the same kind of addition. (2) The results show that the production of a definite equilibrium furnishes an admirable test of the purity of an $\alpha\beta$- or $\beta\gamma$-unsaturated acid: the presence of any impurity (other than the isomeride) in such an acid will be shown by the inability of the sample to yield the correct equilibrium, which can be determined if only one of the two isomerides is available in a state of purity. An application is furnished by the pentenoic acids, for the $\beta\gamma$-acid yields the correct equilibrium value

and therefore contains no $\gamma\delta$-acid ; hence 1 : 2-addition of hydrogen to vinylacrylic acid does not occur.

Synthesis of Pyroterebic Acid.—As shown in Table I, the equilibrium between the γ-methylpentenoic acids is 94·4% $\beta\gamma$- $\rightleftharpoons$ 5·6% $\alpha\beta$- ; this is so one-sided that the pure $\beta\gamma$-acid can readily be prepared from the equilibrium mixture by fractionation under reduced pressure, and pyroterebic acid can thus be obtained from its $\alpha\beta$-isomeride in 75% yield. As the latter acid can very easily be prepared from *iso*butaldehyde, the advantages of this method over those previously reported are obvious. The authenticity of the pyroterebic acid was checked by the preparation of derivatives, by oxidation, and by the determination of its iodine addition value, which agrees with the figure obtained for the acid prepared from terebic acid.

The Mobility of the Acids.—The mobility of the acids studied in this work was in every case greater than that of the *cyclo*hexenylacetic acids, in which series equilibrium was only reached after 21 hours' treatment under the standard conditions. As calculated from the equation previously used (*J.*, 1927, 2579), but multiplying the results by 10 for convenience (instead of by 100, as formerly), the values for $10(k_1 + k_2)$ are : *cyclo*pentenylacetic acids 22, α-methylpentenoic acids 7, γ-methylpentenoic acids 4·5. The mobilities of the hexenoic and of the pentenoic acids (Figs. 1 and 2) are of the same order, about 7. These figures, calculated from the results given on p. 2358, serve to illustrate the important point, also made clear in the graphs, that alkyl substituents have little effect on the mobility of the change, if reversible, although a gradual decrease in mobility is to be expected with increase in molecular weight. The only exception lies in the large difference between the *cyclo*pentenylacetic acids (mobility = 22) and the *cyclo*hexenyl homologues (mobility = 1); this had been foreshadowed by earlier results, for it had been shown (Kon and Linstead, *loc. cit.*) that *cyclo*pentylideneacetic acid was completely equilibrated in less than 10 minutes with boiling 60% caustic potash, whereas the corresponding *cyclo*hexane acid required an hour's treatment under these conditions.

The Effect of Alkyl Substituents on Equilibrium.

The results so far obtained from the study of simple mono-olefinic acids containing no second unsaturated group * are summarised in Table II. (All values are reduced to whole numbers.)

From the figures in Table II, the following generalisations may be drawn regarding the comparative stability of the isomeric acids

* The presence of such groups (*e.g.*, CO_2H,Ph) introduces complicating factors still under study.

TABLE II.

Series of acids.	*Equilibrium*, % $\alpha\beta$-acid.	Series of acids.	*Equilibrium*, % $\alpha\beta$-acid.
β-Methylbutenoic ...	100 [1]	Hexenoic	*ca.* 77
Pentenoic	75	β-Propylhexenoic	34 [3, 4]
α-Methylpentenoic...	81	δ-Methylhexenoic	*ca.* 82 [5]
β- ,, ...	26 [2]	β-*iso*Butyl-δ-methylhexenoic	49 [3, 4]
γ- ,, ...	6	Δ^1-*cyclo*Pentenylacetic	14
β-Ethylpentenoic ...	5 [2]	Δ^1-*cyclo*Hexenylacetic	12 [2]
		Δ^1-*cyclo*Heptenylacetic	26 [3]

[1] Kon and Linstead, *loc. cit.* [2] Linstead, J., 1927, 361. [3] Kon and May, J., 1927, 1549. [4] Linstead and May, J., 1927, 2565.

[5] Fittig (*loc. cit.*) obtained a mixture of unsaturated acids of this composition by the action of alkali on Δ^{α}-*iso*heptenoic acid, and this probably represents an equilibrium value.

towards equilibrating agents (alkyl substituents only are referred to throughout): (1) Butenoic acids without γ-substituents show no stability of the $\beta\gamma$-form even when substituted on the β-carbon atom. (2) Butenoic acids with one γ-substituent show a small but definite stability of the $\beta\gamma$-form, which is not appreciably affected by the nature of the substituent or by the presence of α-substituents. (3) γ-Substituted butenoic acids having a second alkyl group on the γ-carbon show great stability of the $\beta\gamma$-form, and a similar but weaker effect is produced if the second substituent is on the β-carbon atom. The maximum effect in the β-position is given by an ethyl group. (4) These principles are still valid if the substituting groups form part of a polymethylene ring.

No exceptions to these rules are known at present, and it may therefore be predicted that the equilibrium in the methyl*cyclo*hexenylacetic acids derived from *o*-methyl*cyclo*hexanone will be more on the $\beta\gamma$-side than that in the *m*- and *p*-homologues; that di*iso*propylacrylic acid will give a much higher proportion of the $\beta\gamma$-isomeride on equilibration than di-*n*-propylacrylic acid; and that the acrylic acid derived from methyl *iso*propyl ketone will be converted almost completely into its $\beta\gamma$-isomeride on suitable treatment with alkali. It is hoped to test these predictions in the near future.

The theoretical significance of these results is obvious, particularly in the light of the electronic hypothesis of three-carbon tautomerism (Ingold, Shoppee, and Thorpe, J., 1926, 1477; Ingold, *Ann. Reports*, 1927, **24**, 109), but consideration of this point is reserved for a future communication.

EXPERIMENTAL.

A. *Preparation, Purification, and Characterisation of the Acids.*

Δ^{α}-*Pentenoic Acid* (II; $R_{\alpha,\beta,\gamma} = H$).—This was prepared from propaldehyde by the Döbner reaction, pyridine containing ½% of

piperidine being used as condensing agent; it had b. p. 105°/19 mm., m. p. 8° (compare von Auwers, *Annalen*, 1923, **432**, 46). Its identity was confirmed by the preparation of the acid chloride, b. p. 51°/24 mm., dibromide, m. p. 56°, and anilide, m. p. 100° (Wohlgemuth, *Ann. Chim.*, 1914, **2**, 332, gives 99°).

Δ^{β}-*Pentenoic acid* (I; $R_{\alpha,\beta,\gamma} = H$).—Vinylacrylic acid, prepared by the method of Kohler and Butler (*J. Amer. Chem. Soc.*, 1926, **48**, 1036), was purified by washing with light petroleum until it melted at 80° and was then immediately reduced with sodium amalgam by the method of Thiele and Jehn (*Ber.*, 1902, **35**, 2320), a 60% yield being obtained of the pure acid, b. p. 98°/19 mm. The acid chloride, b. p. 46°/23 mm., dibromide, m. p. 64° (Thiele gives 65°), and anilide, m. p. 75° (Wohlgemuth gives 73°) were prepared.

Δ^{α}-*Hexenoic Acid.*—This was prepared from *n*-butaldehyde by the method used for the lower homologue. The pure acid, flattened needles from alcohol, m. p. 32°, was obtained in 60% yield. The dibromide, m. p. 70°, and acid chloride, b. p. 70°/23 mm., were prepared. The latter was converted into the *anilide*, needles, m. p. 109—110° (Found: N, 7·5. $C_{12}H_{15}ON$ requires N, 7·4%).

Δ^{β}-*Hexenoic Acid* (Hydrosorbic Acid).—Sorbic acid was prepared from crotonaldehyde by the method of Döbner (*Ber.*, 1900, **33**, 2140), and the product (yield 35%) had m. p. above 132°. The reduction was carried out in the first place under the conditions used for vinylacrylic acid: Sorbic acid (25 g.), suspended in cold water (2 l.), was treated with 1300 g. of 3% sodium amalgam, the solution being kept neutral by passage of carbon dioxide. At the end of the reaction, the solution was decanted from the mercury, acidified with dilute sulphuric acid and extracted with ether. The product, after drying and removal of the solvent, gave a colourless, rancid-smelling oil, b. p. 98°/9 mm.; $n_D^{19°}$ 1·4398, $d_4^{19°}$ 0·9632, $[R_L]_D = 31·21$; yield, 18 g., 72%. This substance gave an acid chloride, b. p. 52°/18 mm., and an anilide, needles, which in spite of recrystallisation from a variety of solvents melted at about 55° (Auwers and Henya, *loc. cit.*, give 54—56°) (Found: N, 7·3. Calc.: N, 7·4%). A solid dibromide could not be obtained. The acid added on 61·6% of iodine under the standard conditions, and, after equilibration, 47·6% (see p. 2358).

5 G. of the acid were dissolved in chloroform (30 c.c.) and treated with ozonised oxygen for 12 hours; the ozonide was freed from solvent and decomposed by water. The evolved gases were led through a solution of *p*-nitrophenylhydrazine in excess of dilute hydrochloric acid, and the thick, orange precipitate, after recrystallisation, melted at 117°: mixed with an authentic sample of acetaldehyde-*p*-nitrophenylhydrazone (m. p. 126°) it melted at 120°,

whereas the mixed m. p. with *propionaldehyde-p-nitrophenyl-hydrazone* (m. p. 118°) was 114°. When all the aldehyde had been evolved the residue was treated with perhydrol (20 c.c.) and allowed to stand over-night. On evaporation the solution gave succinic acid, m. p. 183° (Found : *M*, by titration, 119. Calc. : *M*, 118), which was further identified by a mixed m. p. determination.

Another sample (5 g.), prepared by the same method, was dissolved in 500 c.c. of water, excess of sodium bicarbonate was added, and the solution was treated slowly with 22 g. of potassium permanganate and 12 g. of magnesium sulphate in 750 c.c. of water. A further quantity of 7·1 g. of permanganate and 15 g. of magnesium sulphate was subsequently added (6 g.-atoms + 5%, in all). The product was worked up in the usual way, and the acid fraction yielded 2·55 g. of a semi-solid residue. The liquid portion of this (0·68 g.) was separated by filtration and converted into the acid chloride with phosphorus trichloride. Some two-thirds of this boiled between 50° and 60° and yielded aceto-*p*-toluidide on reaction with *p*-toluidine. The last few drops of the remaining liquid (b. p. about 75°) were also converted into a *p*-toluidide and gave bold needles of propion-*p*-toluidide, m. p. 123°, from light petroleum. The residual solid acid was succinic acid, m. p. 182°. The identities of these products were confirmed by mixed m. p. determinations.

Modified Reductions of Sorbic Acid.—(1) The reaction was carried out as before, except that dilute sulphuric acid was added at half-hour intervals until the solution was *slightly* acid (compare Fittig and Baker, *loc. cit.*). The product obtained as before boiled at 98—99°/9 mm., and had an "iodine value" of 57·3%, which after equilibration for 48 hours fell to 49·0%. Another sample had b. p. 204—206°/760 mm. and gave a *p*-toluidide forming well-defined tufts of needles, m. p. 74° (indefinite). The cadmium salt (compare Fichter, *Ber.*, 1896, **29**, 2367) was extracted with cold water until one-third remained as residue, and the solution, which should have contained the more soluble salt of the βγ-acid, was evaporated to dryness. The acid was extracted from the residue by treatment with dilute sulphuric acid and ether; it boiled constantly at 101·5°/12 mm. and had $n_D^{18^\circ}$ 1·4405, $d_4^{18^\circ}$ 0·9640, whence $[R_L]_D$ 31·23 (v. Auwers, *loc. cit.*, finds b. p. 112°/10 mm., $n_D^{20^\circ}$ 1·4394, $d_4^{20^\circ}$ 0·9655, $[R_L]_D$ = 31·11); it did not solidify in a freezing mixture, and gave an acid chloride, b. p. 50—51°/14 mm., and an anilide, m. p. 52—56°.

(2) Acetic acid was added during the reduction at such a rate as to keep the solution slightly *acid* throughout. In this way it was hoped to obtain addition of hydrogen to the molecule of sorbic acid as distinct from the ion. The product boiled at 101°/11 mm. and

had an "iodine value" of 52·6%, which fell to 48·9% after equilibration for 48 hours.

(3) Sorbic acid (10 g.), dissolved in moist ether (2000 c.c.), was reduced with aluminium amalgam (20 g.) in the usual way. The product yielded 2 g. of the pure reduced acid, b. p. 102°/12 mm., iodine value 59·8%, falling on equilibration for 48 hours to 50·6%. A considerable quantity of unchanged sorbic acid was recovered from the higher-boiling fractions.

γ-Methyl-Δ^α-pentenoic Acid (Δ^{α}-*iso*Hexenoic acid) (II; $R_{\alpha,\beta}$ =H, R_{γ} = Me).—This was prepared from *iso*butaldehyde by the method used for Δ^{α}-pentenoic acid. After refractionation of the product, the pure acid was obtained in 66% yield; b. p. 113°/20 mm., 104°/10 mm. The *acid chloride* boiled at 67°/20 mm.; the *anilide* crystallised in fine needles from aqueous alcohol, m. p. 119° (Found: N, 7·4. $C_{12}H_{15}ON$ requires N, 7·4%); the *dibromide* crystallised in heavy white cubes, m. p. 124°.

Terebic Acid.—(1) Ethyl diaterebate was hydrolysed with concentrated hydrochloric acid (Simonsen, J., 1907, **91**, 184) but gave a poor yield, never exceeding 20% of terebic acid. Hydrolysis with 50% sodium hydroxide was very violent, but the use of potassium hydroxide gave better results: Ethyl diaterebate (30 g.) was poured into 50% aqueous potassium hydroxide solution (100 c.c.); hydrolysis, which was accompanied by the evolution of much heat, was completed by an hour's heating on the steam-bath, the solution was cooled, the unchanged ester extracted with ether, and the alkaline liquid acidified with concentrated hydrochloric acid and evaporated to dryness. The solid residue was exhaustively extracted with ether in a Soxhlet apparatus, and the solid obtained was repeatedly recrystallised from water. It melted between 162° and 166° and probably contained much teraconic acid. After being heated with concentrated hydrochloric acid and recrystallised, pure terebic acid was obtained, m. p. 175°; yield, nearly 50%.

(2) Ethyl carbethoxysuccinate was prepared in 60% yield by the action of ethyl chloroacetate on ethyl sodiomalonate; its sodio-compound readily reacted with *iso*propyl iodide and gave a 65% yield of ethyl α-carbethoxy-α-*iso*propylsuccinate, b. p. 153—155°/10 mm. This was boiled over-night under reflux with seven times its volume of concentrated hydrochloric acid, and the resulting solution gave *iso*propylsuccinic acid on evaporation to small volume, m. p. 110°; yield, 86%. This acid, when oxidised by the method of Lawrence (J., 1899, **75**, 527), yielded 51% of terebic acid, which melted sharply at 175° after one crystallisation from hot water, together with 20% of the unchanged starting material.

(3) Teraconic acid (Stobbe, *Ber.*, 1893, **26**, 2314) was converted

into terebic acid by boiling over-night with concentrated hydrochloric acid under reflux (compare Fittig and Frost, *Annalen*, 1884, **226**, 365), a 90% yield being obtained.

γ-Methyl-Δ^{β}-pentenoic Acid (Pyroterebic Acid) (I; $R_{\alpha,\beta} = H$, $R_{\gamma} = Me$).—(1) *By dry distillation of terebic acid.* The method of Fittig and Geisler (*Annalen*, 1881, **208**, 37) was improved as follows: Terebic acid, in 20 g. portions, was placed in a 100 c.c. distilling flask fitted with a thermometer, the bulb of which almost touched the bottom of the flask. To the side arm was attached a 50 c.c. distilling flask and to the side arm of this a small water condenser in a vertical position. The acid was heated *as quickly as possible* to 240°. At 175—180° it melted to a clear golden oil, and at about 240° water began to separate. The oil then distilled without charring. The distillate partly solidified on cooling, owing to the presence of unchanged terebic acid. It was distilled in steam, terebic acid and teraconic acid (2·8 g.) being left in the residue. The aqueous distillate was saturated with sodium bicarbonate and extracted with ether to remove *iso*caprolactone (0·5 g.). The alkaline solution was then acidified and extracted thoroughly with ether. The product, isolated after removal of the solvent and refractionation, distilled at 99°/10 mm.; yield, 6·5 g. (33%). The *acid chloride* boiled at 60°/15 mm. The *anilide* crystallised from alcohol and water in needles, m. p. 106° (Found : N, 7·5. $C_{12}H_{15}ON$ requires N, 7·4%). The dibromide was obtained as hard white crystals, m. p. 99°.

(2) *From* Δ^{α}-iso*hexenoic acid.* The αβ-acid (20 g.) was heated for 15 hours with a solution of potassium hydroxide (120 g.) in 250 c.c. of water. The solution was cooled, acidified, and extracted thoroughly with ether. After removal of the ether, the residual oil was distilled in steam and extracted as in the previous method. Almost the whole product distilled at 99—100°/10 mm., the last fractions, about 2 c.c., being rejected. On refractionation, 15 g. of a clear colourless oil were obtained, b. p. 99°/10 mm. (75% yield). This preparation gave the following derivatives: acid chloride, b. p. 62°/16 mm.; anilide, in needles from benzene–light petroleum, m. p. 104° [mixed m. p. with the αβ-anilide (of m. p. 119°) 85—87°; mixed m. p. with anilide prepared by method (1) 106°]; dibromide, m. p. 99°, not depressed in admixture with dibromide from preparation (1).

The new acid (5 g.), dissolved in dry chloroform (30 c.c.), was treated with dry ozonised oxygen for 20 hours; the precipitated white, solid *ozonide*, sparingly soluble in chloroform, had m. p. 110° (decomp.) after drying in a vacuum. A portion of the ozonide was treated with an excess of water, and the aldehyde evolved was

converted into the *p*-nitrophenylhydrazone; this formed yellow needles from alcohol, m. p. 126°, and was identified as the acetaldehyde derivative by comparison with an authentic sample: a mixture with a specimen of the *p*-nitrophenylhydrazone of *iso*butaldehyde (m. p. 128°) melted at 103°. When all the acetaldehyde had been removed, the residual solution was heated under reflux for an hour, and a white, crystalline deposit was formed in the condenser. An excess of sodium bicarbonate was added and the liquor slowly distilled under a column, the first 10 c.c. being collected. The presence of acetone in this was shown by the immediate formation of iodoform and by the preparation from it of dibenzylidene-acetone (m. p. 111°, identified by mixed m. p.). The white solid, volatile in steam, was undoubtedly acetone superoxide.

The remainder of the ozonide was left over-night with an excess of perhydrol, and the solution subsequently evaporated to small bulk; malonic acid crystallised on cooling, and was identified by its m. p. (129°), by its decomposition to acetic acid, and by a mixed m. p. determination.

α-Methyl-Δ^{α}-pentenoic Acid (II; R_{α} = Me, $R_{\beta,\gamma}$ = H).—α-Methyl-β-ethylacrolein (Döbner and Weissenborn, *Ber.*, 1902, **35**, 1144) was distilled, and the fraction of b. p. 55—60°/18 mm. was immediately oxidised. The aldehyde (40 g.), mixed with silver nitrate (230 g.), water (500 g.), and rectified spirit (200 c.c.), was stirred vigorously, and to it were added during 3 hours 75 g. of sodium hydroxide in 1 litre of water (compare Delépine and Bonnet, *loc. cit.*); reaction was completed by standing over-night. The filtered solution was acidified and thoroughly extracted with ether. The product, after drying and removal of the solvent, was fractionated, α-methyl-Δ^{α}-pentenoic acid being obtained as a colourless oil, b. p. 112°/12 mm. (yield, 25 g., 60%). On cooling in ice, the product solidified completely and melted at 22—23° (Lieben and Zeisel, *Monatsh.*, 1883, **4**, 46, give 24·4°).

The *acid chloride* boiled at 63°/16 mm. The *amide*, prepared from this by the action of dry ammonia in benzene solution, crystallised from benzene or carbon disulphide in plates, m. p. 80° (Found: N, 12·3. $C_6H_{11}ON$ requires N, 12·4%). All the crops obtained by fractional crystallisation of this substance melted sharply at 80°, and the m. p. could not be raised by further purification; we were unable therefore to obtain either of the amides, m. p. 65·5° and 96°, described by Macq (*Bull. Acad. roy. Belg.*, 1926, **12**, 753) as those of the *cis*- and *trans*-forms of this acid. The preparative method used by Macq (hydrolysis of the corresponding unsaturated nitrile) would, however, certainly lead to the production of a mixture, and it is probable that this was insufficiently separated (com-

pare Newbery, J., 1925, **127**, 295; von Auwers, *Annalen*, 1923, **432**, 46).

The *anilide* of α-methyl-Δ^{α}-pentenoic acid, prepared from the acid chloride, crystallised from benzene–light petroleum in needles, m. p. 84° (Found : N, 7·2. $C_{12}H_{15}ON$ requires N, 7·4%). The dibromide crystallised from carbon disulphide in hard, white prisms, m. p. 96—97° (Lieben and Zeisel, *loc. cit.*, p. 77, give 97·6°).

α-Methyl-Δ^{β}-pentenoic Acid (I; R_{α} = Me, $R_{\beta,\gamma}$ = H).—This was prepared by the method of Fichter and Rudin (*Ber.*, 1904, **37**, 1615), who, however, gave scanty details. Ethyl α-methyl-β-acetosuccinate (100 g.), obtained in 62% yield from ethyl sodioacetoacetate and ethyl α-bromopropionate, was dissolved in 200 c.c. of rectified spirit and 150 c.c. of water, and cooled to 0°. To the mechanically stirred solution were added 1400 g. of 3% sodium amalgam in seven equal lots at one-hour intervals, 100 c.c. of water being added with each addition. The solution was kept over-night and the supernatant liquor separated from the mercury, carefully acidified with dilute sulphuric acid (evolution of carbon dioxide) and extracted with ether. The extract was dried and the residue after removal of the solvent was fractionated in a vacuum. The low-boiling fraction, 140—160°/12 mm. (15 g.), was presumably α-methyllævulic acid. At 195°/12 mm., αγ-dimethylparaconic acid, $CH_3\cdot CH\cdot CH(CO_2H)\cdot CHMe\cdot CO$ (└——O——┘), came over and solidified to a mass of long, white crystals (30 g., 40%), m. p. 130° after crystallisation (Fichter and Rudin report a 70% yield, but we were unable to obtain this in spite of many variations of conditions).

The paraconic acid (20 g.) was distilled from the same apparatus as that used for terebic acid, the temperature being raised *very gradually* to 240°; distillation commenced at 280° and continued up to 285°, there being no charring of the paraconic acid. The product was worked up as described for pyroterebic acid, and on fractionation gave 7·5 g. of a liquid, b. p. 101—103°/16 mm., and 102°/16 mm. after refractionation; yield, 33%. From the residue of the steam-distillation, 3 g. of the paraconic acid were recovered. Fichter and Rudin (*loc. cit.*), using a different method of separation, obtained only 16% of the unsaturated acid.

The *acid chloride* boiled at 47°/17 mm. The *amide*, prepared in the same way as the αβ-isomeride, crystallised from carbon disulphide or benzene in glistening plates, m. p. 74° (Found : N, 12·2. $C_6H_{11}ON$ requires N, 12·4%). The *anilide* crystallised from aqueous alcohol or benzene–light petroleum in needles, m. p. 76° (Found : N, 7·4. $C_{12}H_{15}ON$ requires N, 7·4%).

cyclo*Pentylideneacetic acid* (IV) (Kon and Linstead, *loc. cit.*)

boiled at 133°/15 mm. and solidified to a white mass which on crystallisation from alcohol melted sharply at 64°.

Δ^1-cyclo*Pentenylacetic acid* (III) was prepared by the action of a large excess of 40% potassium hydroxide on the αβ-isomeride for 1 hour. The acid, isolated in the usual way, was freed from adhering oil by washing with light petroleum, and recrystallised from aqueous alcohol, m. p. 52°; yield, 50%.

B. *Equilibration of the Acids.*

The same potassium hydroxide solution was used throughout: it contained 300 g. KOH per litre of solution, and was standardised from time to time against *N*-acid. Equilibrations were carried out by the standard procedure (J., 1927, 2579), 2 g. of the acid being sealed up with exactly ten times the theoretical amount of the alkali. The reaction mixture was then heated in a bath of boiling water. Owing to the formation of hydroxy-acids, the method of working up the product differed from that used previously. At the end of the required time the tube was opened and the contents were acidified and extracted with ether. The undried extract was freed from solvent under a good column and slowly distilled in steam for 1 hour. The mixed unsaturated acids in the distillate (about 1 litre) were isolated in the usual way after removal of lactone. The residual oil was washed into a tared beaker with pure ether and weighed after removal of the ether in a vacuum over paraffin wax. In every case about 1·7 g. of mixed acids (*ca.* 85%) were recovered in this way.

The residue from the distillation in steam was extracted with ether and the hydroxy-acids were isolated, after drying and removal of the solvent, as sweet-smelling viscous oils. The following amounts were obtained during the equilibrations: Pentenoic acids, traces; hexenoic acid, 22%; *iso*hexenoic acid, 5%; α-methylpentenoic acids, traces; *cyclo*pentenyl acids, nil.

The molecular weight of the β-hydroxy-*n*-caproic acid derived from Δ^α-hexenoic acid was found by titration with standard baryta to be 131 ($C_6H_{12}O_3$ requires 132). The other hydroxy-acids were not obtained in quantities sufficient for examination. In this respect the results are contrasted with those of Fittig, who obtained quantities of β-hydroxy-acids varying from 15 to 35%.

C. *Analysis of the Equilibrated Acids.*

The method of Linstead and May (*loc. cit.*) was used throughout. Data for reference were first obtained by determining the % addition of iodine under the standard conditions to mixtures of the isomerides of known composition, at least three determinations being made

on every mixture. These data were then incorporated into reference curves, this "iodine value" being plotted against the % composition of the mixed acids. Quantities of the equilibrated acids equivalent to $M/300$ were then examined in the same way, three determinations of the iodine value being made in each case. The composition of the acid mixture was then found from the reference curve. The time of equilibration was increased until there was no further change in the iodine value of the product. The curves obtained from each pair of isomerides by plotting time of equilibration against composition of the product were of the exponential type, becoming asymptotic to each other at the equilibrium point (Figs. 1 and 2).

The *following tables summarise this section of the experimental* work.

Pentenoic acids : Reference data.

% αβ-Acid	100	80	66·6	50	33·3	20	0
Iodine value (10 mins.)	4·4	13·7	19·8	26·6	34·8	41·4	46·8

Equilibration data.

Starting acid :	αβ.	αβ.	αβ.	αβ.	βγ.	βγ.	βγ.	βγ.
Time of reaction (hrs.)	1½	4½	12	16½	½	1½	7½	17
Iodine value	9·8	15·7	15·8	15·9	22·5	17·4	15·7	15·8
% αβ-Acid	88·8	75·6	75·4	75·2	61·6	72·3	75·6	75·4

Mean iodine value at equilibrium : 15·8. αβ-Acid = 75·4%.

n-*Hexenoic acids.*

Iodine value for αβ-acid 1·4%, for βγ-acid (estimated) 70%.

Equilibration data.

Starting acid :	αβ.	αβ.	αβ.	αβ.	αβ.	βγ.*	βγ.	βγ.	βγ.	βγ.
Time of reaction (hrs.)	1	2	4	6	8	1½	2	4	21	24
Iodine value	14·3	18·4	19·9	20·0	19·9	61·6	61·6	52·6	47·4	47·8

* Hydrosorbic acid prepared by first method : iodine value 61·6%. The variation in the iodine values of other samples of hydrosorbic acid on equilibration has already been given (p. 2352).

Since the pure hydrosorbic (βγ-)acid was not obtained in the course of this work the position of equilibrium could only be determined approximately. It will be noticed from the figures given on p. 2352 that the samples of mixed βγ- and γδ-hexenoic acids which gave the lowest iodine values were also those whose iodine values *changed least on equilibration*, *i.e.*, were those containing the most γδ-acid. From a study of these results, we deduce that the iodine values of the βγ- and γδ-acids are approximately 70 and 50%, respectively, and assuming this figure for the pure βγ-acid, the equilibrium is of the order 22% βγ : 78% αβ. This equilibrium was also deter-

mined by Bougault's method (*Ann. Chim. Phys.*, 1908, **14**, 145), the unchanged αβ-acid being actually isolated (Linstead and May, *loc. cit.*). In three experiments, from 2 g. of the equilibrium mixture there were isolated 1·44 g., 1·60 g., and 1·57 g. of the solid αβ-acid, which give a mean value for the equilibrium of 77% αβ : 23% βγ. The variation in the above figures shows, however, that the method is by no means accurate.

γ-Methylpentenoic acids : Reference data.

% αβ-Acid	100	80	60	40	20	0*	0†
Iodine value (5 mins.)	1·8	17·8	34·2	49·0	63·1	73·4	73·1

Equilibration data.

Starting acid :	αβ.	αβ.	αβ.	αβ.	αβ.	βγ.*	βγ.†
Time of reaction (hrs.)	1¼	3¼	6½	15	26	5	5
Iodine value (5 mins.)	33·0	60·2	71·1	71·6	71·4	71·4	70·9
% αβ-Acid	61·8	24·5	6·0	5·1	5·4	5·4	6·3

Mean iodine value at equilibrium : 71·3. αβ-Acid = 5·6%.

* Pyroterebic acid from terebic acid. † Pyroterebic acid from αβ-acid.

The reaction of γ-methyl-Δ^{β}-pentenoic acid with iodine under the conditions was very rapid at first but appeared to stop after 5 minutes.

α-Methylpentenoic acids : Reference data.

% αβ-Acid	100	80	60	40	20	0
Iodine value (10 mins.)	0	11·1	21·0	30·5	39·9	44·1

Equilibration data.

Starting acid :	αβ.	αβ.	αβ.	αβ.	αβ.	βγ.	βγ.	βγ.
Time of reaction (hrs.)	1	2	4½	6	10	1	4½	7
Iodine value (10 mins.)	3·7	7·75	10·6	11·0	10·8	25·8	10·4	10·7
% αβ-Acid	93·9	87·0	80·9	80·2	80·5	50·5	81·2	80·7

Mean iodine value at equilibrium : 10·7. αβ-Acid = 80·7%.

cyclo*Pentenylacetic acids : Reference data.*

% αβ-Acid	100	80	66·6	50	33·3	20	0
Iodine value (10 mins.)	12·8	34·0	45·2	58·3	72·6	80·3	87·7

Equilibration data.

Starting acid :	αβ.	αβ.	αβ.	αβ.	αβ.	αβ.	αβ.	αβ.	βγ.
Time of reaction (hrs.) ...	¼	½	1	2	4	6	8	10	2
Iodine value (10 mins.)...	47·8	61·0	81·4	82·6	83·4	83·5	83·4	83·4	83·4
% αβ-Acid	64·3	49·0	18·7	15·6	13·7	13·5	13·7	13·7	13·7

Mean iodine value at equilibrium : 83·4. αβ-Acid = 13·7%.

In this series, the residual iodine was titrated with thiosulphate without previous acidification, and there is a slight absolute error

which does not extend to the interconversion curves and the position of equilibrium.

Much of the heavy cost of this investigation has been defrayed by grants from the Government Grant Committee of the Royal Society and from the Chemical Society, to whom we wish to acknowledge our indebtedness. Our thanks are also due to Professor J. F. Thorpe, F.R.S., and Dr. G. A. R. Kon for their interest in the progress of the work.

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CCCXI.—*On the Possibility of Ring-chain Valency Tautomerism and of a Type of Mobile-hydrogen Tautomerism analogous to the Wagner–Meerwein Rearrangement. Part IV. Substitution Reactions of some Cyclic Derivatives of Phorone.*

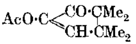
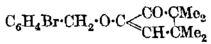
By CHARLES WILLIAM SHOPPEE.

IN the course of previous investigations (Francis and Willson, J., 1913, **103**, 2238; Ingold and Shoppee, this vol., p. 365) on the cyclic phorone derivatives represented by the formulæ (I) and (II), numerous observations have been made which indicate that the 5-carbon nucleus possesses remarkable stability such as is sometimes found to be associated with tautomeric complexes. Reference may be made to the smooth formation of bromohydroxyphorone (X = O, Y = Br) by the action of concentrated sulphuric acid on dibromophorone and by the action of bromine and water on 3 : 3 : 4 : 4-tetramethyl*cyclo*pentanone; to the conversion of hydroxyphorone (Y = H) into the bromohydroxy-compound by direct bromination without detectable intermediate addition; to the direct reduction of derivatives of bromohydroxyphorone to corresponding derivatives of hydroxyphorone without loss of the unsaturation on which tautomeric character depends; and finally to the stability towards brominating, reducing, and certain oxidising agents of some of the derivatives of hydroxy- and bromohydroxy-phorone. These observations call to mind the properties of the *gem*-dialkyl*cyclo*pentadiene nucleus investigated by Farmer, Ingold, and Thorpe (J., 1922, **121**, 128), and the analogy between compounds containing this nucleus and aromatic substances (Ingold, Seeley, and Thorpe, J., 1923, **123**, 852); it was therefore decided to study the action of substituting agents on hydroxyphorone and its derivatives in order

to determine the conditions under which the nuclear type is preserved.

(I.) (II.)

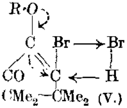
By the action of bromine in chloroform upon the acetoxy-compound (III) and the methoxy- and *p*-bromobenzyloxy-compounds represented by (IV), bromohydroxyphorone was produced. Hydrogen bromide was evolved from the commencement of the reaction and no evidence was obtained of intervening bromine

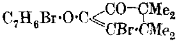
(III.)   (IV.)

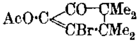
addition. The fact that the alkyl and acyl groups are eliminated in the course of these reactions places difficulties in the way of their interpretation, since it is not known whether the eliminations are antecedent or subsequent to the nuclear substitution; if they are antecedent, substitution might occur through the ion of hydroxyphorone with the formation of a tautomeride of the product isolated (compare Part I, p. 383):

The facility with which this reaction would be expected to occur is such that, assuming the elimination of the *O*-substituent to be brought about by hydrogen bromide, a very small amount of fission at the commencement of the reaction would suffice to cause the whole of the subsequent process to pursue the course indicated. This mechanism is not analogous to the general case of substitution in the aromatic series, and the behaviour of other halogenating agents was therefore investigated. Quinolinium perbromide also causes the elimination of the acetyl group from the acetoxy-compound (III) and yields the same bromination product as that obtained by means of bromine. In the case of the *p*-bromobenzyloxy-compound (IV), however, fission did not take place and simple nuclear substitution was observed, the product being (VI). A similar result was achieved in the formation of (VII) from the acetoxy-compound (III) by brominating with quinolinium perbromide in the presence of a quantity of quinoline sufficient to prevent the formation of free hydrogen bromide during the process. These substitutions cannot involve prior ionisation of the organic

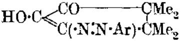
molecule and are regarded as taking the course indicated in formula (V).

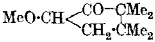

(V.)


(VI.)


(VII.)

The acyl and alkyl derivatives mentioned above appear to show but little tendency to couple with diazonium salts, but hydroxyphorone readily does so, and it is therefore assumed that in this case the reaction occurs through the anion. Deep red dyes of the type (VIII) have been prepared from hydroxyphorone and several aromatic diazonium salts. The position of coupling was indicated in the first place by the fact that the reaction fails with bromohydroxyphorone, and was definitely proved by complete reduction of the dye given by *p*-carbethoxybenzenediazonium sulphate. Hydrolysis of the carbethoxy-group present in one of the pair of bases formed by reduction enabled the aliphatic constituent to be separated and this was then identified as 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine.

(VIII.) 

 (IX.)

In the above examples, the nuclear form originally present is preserved throughout the substitution, and it became of interest to ascertain whether, if the type were destroyed by previous rednction, it would be regenerated during halogenation. For this purpose, the saturated methoxy-compound (IX) was prepared, and when it was subjected to the action of bromine and chloroform, the tautomeric bromohydroxy-compound was produced.

EXPERIMENTAL.

Bromination with Free Bromine in Chloroform Solution.—5-*Acetoxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^4-cyclo*pentenone*. The substance, b. p. 120—121°/10 mm., reacted readily at 35° with one molecular proportion of bromine, evolution of hydrogen bromide taking place. The residual oil, obtained after removal of the solvent on the steam-bath, readily solidified; it was pressed on porous tile and crystallised from ligroin (b. p. 80—100°), from which it separated in colourless needles, m. p. 116°, identified as bromohydroxyphorone by direct comparison and mixed melting point.

5-*Methoxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^4-cyclo*pentenone*. The pure methoxy-derivative, prepared by methylating the hydroxy-ketone, b. p. 110°/18 mm., was treated with 1 mol. of bromine; substitution

with evolution of hydrogen bromide occurred readily on gentle warming. The product, bromohydroxyphorone, m. p. 116°, was isolated and identified as above.

5 - p - *Bromobenzyloxy* - 2 : 2 : 3 : 3 - *tetramethyl* - Δ^4 - cyclo*pentenone*. The crystalline solid, m. p. 86°, was treated with 1·2 mols. of bromine in boiling chloroform, and substitution slowly took place. When evolution of hydrogen bromide had ceased, the solvent and the excess of bromine were removed on the steam-bath. The residual oil, which was lachrymatory and had the characteristic odour of *p*-bromobenzyl bromide, solidified on stirring, and was washed with a little hot ligroin (b. p. 40—60°) to remove this product. The solid was crystallised from ligroin (b. p. 80—100°) and then it had m. p. 116°; it was identified as before.

5-*Methoxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanone*. The methoxy-compound was treated with excess of bromine in hot chloroform, substitution taking place with evolution of hydrogen bromide. The solvent, excess of bromine, and hydrogen bromide were removed on the steam-bath and the residual oil soon became solid. It was identified as bromohydroxyphorone. In another experiment, bromine (1 mol.) was added to the warm chloroform solution of the methoxy-compound. Substitution took place after a short induction period, and bromine was added until a permanent red colour was obtained. The residue remaining after evaporation partially crystallised, and the solid separated from ligroin (b. p. 60—80°) in colourless prisms, m. p. 99—100° The *dibromo*-compound gave no colour with aqueous-alcoholic ferric chloride, and was stable to bromine in acetic acid, and to alkaline permanganate; on keeping it decomposed with evolution of free bromine (Found: C, 37·1, 37·3; H, 5·6, 5·8. $C_{10}H_{16}O_2Br_2$ requires C, 36·6; H, 4·9%).

3 : 3 : 4 : 4-*Tetramethyl*cyclo*pentanone*. The ketone was treated with bromine (2 mols.), substitution taking place on gentle warming. The product obtained on evaporation crystallised from ligroin (b. p. 60—80°) in long needles, m. p. 93°, and depressed the m. p. (99—100°) of the substance described above (Found: C, 36·7, 37·2; H, 4·6, 4·4; Br, 53·8, 53·9. $C_9H_{14}OBr_2$ requires C, 36·2; H, 4·7; Br, 53·7%).

5-*Benzoyloxy*-3 : 3 : 4 : 4-*tetramethyl*cyclo*pentanone*. The bromination of this substance (Part II, this vol., p. 1662) has been reinvestigated, but with little success. In addition to free benzoic acid, a bromine-free *substance* is formed, m. p. 100—101°, to which no formula has been assigned (Found: C, 71·3, 71·6; H, 7·4, 7·2%).

Bromination with Quinolinium Perbromide.—The reagent was prepared by the method of Rosenmund and Kühnhenn (*Ber.*, 1923,

56, 1264); alcohol, which these authors recommend for crystallisation, may be advantageously replaced by chloroform.

Acetoxy-derivative (III). (1) The compound was dissolved in glacial acetic acid, and the calculated quantity of quinolinium perbromide added. The whole was warmed on the steam-bath for ¼ hour, during which the red colour of the solution disappeared. On dilution with ice-water, a crystalline precipitate separated; this was filtered off, dried in a vacuum, crystallised from ligroin (b. p. 80—100°), and identified as bromohydroxyphorone (yield, 75%).

(2) The above experiment was repeated, but with the addition of quinoline (1 mol.). The product was isolated as described above, and when crystallised from dilute acetic acid had m. p. 73°. It was identified as 4-bromo-5-acetoxy-2 : 2 : 3 : 3-tetramethyl-Δ^4-*cyclo*pentenone by direct comparison and by mixed m. p. (yield, 70%).

p-*Bromobenzyloxy-derivative* (IV). The same product was obtained with or without the presence of free quinoline. After crystallisation from ligroin (b. p. 60—80°), it had m. p. 64°, and did not depress the m. p. (64°) of 4-bromo-5-*p*-bromobenzyloxy-2 : 2 : 3 : 3-tetramethyl-Δ^4-*cyclo*pentenone on admixture (yield, 80%).

Coupling of the Hydroxy-ketone with Diazonium Salts.—With benzenediazonium sulphate the dye produced by coupling was amorphous, but with 2 : 4 : 6-tribromobenzenediazonium sulphate and with *p*-carbethoxybenzenediazonium sulphate, crystalline products were obtained. The diazonium sulphates were prepared according to the method of Knoevenagel (*Ber.*, 1895, **28**, 2049).

4-2′ : 4′ : 6′-*Tribromobenzeneazo-5-hydroxy-2 : 2 : 3 : 3-tetramethyl-*Δ^4-cyclo*pentenone* separates in crimson needles when the theoretical quantity of dry 2 : 4 : 6-tribromobenzenediazonium sulphate, dissolved in aqueous methyl alcohol, is added to the aqueous methyl-alcoholic solution of the hydroxy-ketone. It is soluble in cold 2*N*-sodium hydroxide (Found : C, 36·2; H, 3·1. $C_{15}H_{15}O_2N_2Br_3$ requires C, 36·3; H, 3·0%).

4-p-*Carbethoxybenzeneazo-5-hydroxy-2 : 2 : 3 : 3-tetramethyl-*Δ^4-cyclo*pentenone*, obtained similarly, forms crimson needles, m. p. 160° (decomp.), and is soluble in cold 2*N*-sodium hydroxide (Found : C, 65·4; H, 6·7. $C_{18}H_{22}O_4N_2$ requires C, 65·4; H, 6·7%).

Reduction of the p-*Carbethoxy-dye.*—The substance (2·0 g.) was reduced in hot aqueous-alcoholic solution with successive small quantities of sodium hydrosulphite (5·0 g.). The product, which contained some substance readily oxidised by atmospheric oxygen, was extracted with ether, and the ethereal extract evaporated under a column. The residual oil was boiled with phosphorus and

hydriodic acid (*d* 1·7) for 2 hours to effect reduction of the phorone nucleus and hydrolysis of the *p*-carbethoxy-group. The liquid was then made strongly alkaline and steam-distilled, and the distillate extracted with ether. The ethereal extract was dried with anhydrous potassium carbonate and evaporated under a column. The product was identified as *2 : 2 : 3 : 3-tetramethylcyclopentylamine*; it was accompanied by a trace of some other base yielding a picrate, m. p. 185° (decomp.).

The author wishes to record his thanks to the Royal Commission of 1851 for a Senior Studentship.

THE UNIVERSITY, LEEDS. [*Received, July 21st, 1928.*]

CCCXII.—*An Attempt to prepare Optically Active Derivatives of Quadrivalent Tin.*

By FREDERIC BARRY KIPPING.

THE only optically active compound of tin hitherto described is that of Pope and Peachey (P., 1900, **16**, 42, 116), who obtained externally compensated methylethyl-*n*-propylstannic, iodide, and hence prepared both the *d*-camphorsulphonate and the *d*-α-bromo-π-camphorsulphonate. Evaporation of aqueous solutions of these salts produced in each case salts of the dextrorotatory base only, the whole of the lævorotatory base being converted into its dextrorotatory isomeride. From these salts was isolated *d*-methylethyl-*n*-propylstannic iodide, having $[\alpha]_D = +23°$ in ethereal solution. Furthermore, *d*-methylethyl-*n*-propylstannic *d*-α-bromo-π-camphorsulphonate was found to be completely racemised by heating in aqueous solution on the water-bath for 2 hours, such a solution again giving the dextrorotatory salt on evaporation to dryness.

In view of these results it appeared to be of interest to attempt the preparation of further optically active derivatives of tin in order to ascertain if the remarkable mobility of the groups attached to this atom persisted in all its compounds. The aromatic derivatives were chosen for this investigation, as being more readily crystallised and possibly less easily racemised than the aliphatic compounds. The proposed method of preparation was that of Pope and Peachey, *i.e.*, to start with a triarylstannic halide, introduce a different aryl group by means of the Grignard reagent and remove one of the three original radicals by treatment with iodine:

$$SnPh_3Cl \xrightarrow{BzMgCl} SnPh_3Bz \xrightarrow{I_2} SnPh_2BzI$$

A third aryl group was then to be introduced and one of the two like radicals again removed,

$$SnPh_2BzI \xrightarrow{p\text{-}CH_3\cdot C_6H_4\cdot MgBr} SnPh_2Bz(CH_3\cdot C_6H_4) \xrightarrow{I_2} SnPhBz(CH_3\cdot C_6H_4)I$$

As a preliminary, it was therefore decided to prepare some mixed tin-aryls and study the action of iodine on these compounds in order to determine in which order the various groups must be introduced into the molecule for the above purpose.

The only available data on this subject are that treatment of a benzyl-alkyl compound with iodine results in the elimination of a benzyl group (Smith and Kipping, J., 1912, **101**, 2553), and that one of the phenyl groups is similarly removed from *cyclo*hexyltriphenyl stannane (Krause and Pohland, *Ber.*, 1924, **57**, 544).

In the present instance, it was found that the ease with which various groups were removed by iodine from a molecule containing two or three different radicals decreased in the following order: *o*-tolyl, *p*-tolyl, phenyl, benzyl. Thus triphenyl-*p*-tolylstannane with iodine gave triphenylstannic iodide and *p*-iodotoluene, but *triphenylbenzylstannane* yielded diphenylbenzylstannic iodide and iodobenzene. The tin aryls are also decomposed by boiling with concentrated hydrochloric acid, and it was found that this reagent often removed two aryl groups.

For example, triphenylbenzylstannane yields *phenylbenzylstannic chloride* and benzene, whilst tetraphenylstannane gives diphenylstannic chloride. The order in which the groups were removed by hydrochloric acid was the same as that with iodine, except that, whereas iodine removes one of the benzyl radicals from tribenzylethylstannane, hydrochloric acid removes the ethyl group.

Phenylbenzyl-p-*tolylstannic hydroxide* was then prepared by the following series of reactions:

$$SnPh_4 \xrightarrow{I_2} SnPh_3I \xrightarrow{BzMgCl} SnPh_3Bz \xrightarrow{HCl} SnPhBzCl_2 \xrightarrow{MgBr(p\text{-}CH_3\cdot C_6H_4)}$$
$$SnPhBz(p\text{-}C_7H_7)_2 \xrightarrow{I_2} SnPhBz(p\text{-}C_7H_7)I \xrightarrow{NH_4OH} SnPhBz(p\text{-}C_7H_7)OH$$

and *salts* of this base were prepared with *d*-camphorsulphonic, *d*-α-bromo-π-camphorsulphonic and tartaric acids, but they could not be obtained crystalline.

Phenylbenzyl-n-*butylstannic iodide* was then prepared:

$$SnPh_3Bz \xrightarrow{I_2} SnPh_2BzI \xrightarrow{MgBuBr} SnPh_2BzBu \xrightarrow{I_2} SnPhBzBuI$$
$$\uparrow MgBzCl$$
$$SnPh_3I \xrightarrow{MgBuBr} SnPh_3Bu \xrightarrow{I_2} SnPh_2BuI$$

but again the salts, with the exception of the *fluoride*, proved to be oils. It was then thought that the aromatic nucleus directly

ttached to the tin atom might be the cause of the failure of the salts o crystallise, and a third compound, *benzylethyl*-n-*butylstannic odide*, was prepared in which no nucleus is thus attached :

$$SnBz_3Cl \xrightarrow{MgEtBr} SnBz_3Et \xrightarrow{I_2} SnBz_2EtI \xrightarrow{MgBuBr} SnBz_2EtBu \xrightarrow{I_2} SnBzEtBuI$$

Iere again the salts resisted all attempts at crystallisation.

EXPERIMENTAL.

Phenyltribenzylstannane.—To a solution of phenyl magnesium romide (2 mols.) in ether was added tribenzylstannic chloride 1 mol.) (J., 1912, **101**, 2556), and the mixture heated on the water ath for ½ hour. The ether was then removed by distillation and he heating continued for a further 1½ hours. The product was reated with water, distilled in steam, and the residual oil extracted vith ether, dried, and distilled in a vacuum, b. p. 290°/5 mm.* Found : C, 69·4 ; H, 5·5. $C_{27}H_{26}Sn$ requires C, 69·1 ; H, 5·5 %). *Phenyltribenzylstannane* does not solidify at 0° and is miscible with ll the ordinary solvents, with the exception of alcohol ; it is conerted by boiling concentrated hydrochloric acid into tribenzyltannic chloride and benzene.

Tribenzylstannic iodide was obtained from tribenzylstannic ydroxide (*Z. anorg. Chem.*, 1910, **68**, 102) by warming with dilute ydriodic acid ; it crystallises easily from glacial acetic acid in listening, needle-like prisms, m. p. 102—103° (Found : I,† 24·3 ; Sn, 22·7. $C_{21}H_{21}ISn$ requires I, 24·5 ; Sn, 22·9%). The same ompound was obtained by treatment of phenyltribenzylstannane 1 mol.) dissolved in carbon tetrachloride with iodine (1 mol.), emoval by steam-distillation of the solvent and iodobenzene, and rystallisation from acetic acid.

Dibenzylstannic Chloride.—Attempts to prepare benzylstannic hloride by treatment of tribenzylstannic chloride with 2 mols. of odine resulted in failure, as only one benzyl group could be removed n this way ; the product, isolated in the usual way and converted rom iodide into chloride, proved to be dibenzylstannic chloride, n. p. 158°.

Tetraphenylstannane was prepared in quantity by a modification f the method of Pfeiffer and Schnurmann (*Ber.*, 1904, **37**, 319). Stannic chloride (100 g.) was slowly added to absolute ether (440 c.c.) which was cooled in ice and stirred mechanically. Magnesium

* The pressures given in this paper are probably only accurate to 2—3 mm.

† All halogen determinations were carried out by dissolving the material n alcohol, adding excess of $N/10$-silver nitrate and titrating the excess with otassium thiocyanate.

(36·8 g.) was then added and bromobenzene (244 g.) dropped in slowly. After the addition of the first 10 c.c. or so, a crystal of iodine was added to start the reaction, the mixture being warmed if necessary. The bromobenzene was afterwards added at such a rate that the mixture, still cooled in ice and stirred well, boiled gently. Addition occupied about 1 hour, and the product was then heated on the water-bath for 2 hours, the ether distilled away, and heating continued for a further 2 hours. The solid residue was then add[illegible] to cold water, acidified with hydrochloric acid, and filtered. T[illegible] solid, after drying in air, was boiled with about 600 c.c. of xyl[illegible] and the solution filtered hot. Tetraphenylstannane crystallised from the filtrate in slender needles and was recrystallised from the same solvent; yield about 50—55%.

Triphenylstannic Chloride.—Attempts to prepare this substance directly from stannic chloride (1 mol.) and phenyl magnesium bromide (3 mols.) by a method similar to that used for tribenzylstannic chloride (J., 1912, **101**, 2556) yielded tetraphenylstannane as the principal product, with only small amounts of the halogen compound; the method of Chambers and Scherer (*J. Amer. Chem. Soc.*, 1926, **48**, 1055) was finally found to be best for the preparation of both the chloride and iodide: Tetraphenylstannane was boiled with hydrochloric acid for about 10 mins. and the oily product extracted with petroleum; on standing, a solid mass of diphenylstannic chloride, m. p. 42°, was produced from which, by boiling with water, diphenylstannic hydroxychloride, m. p. 187°, could be prepared.

Triphenylbenzylstannane was prepared from triphenylstannic iodide and benzyl magnesium chloride in the usual manner. After removal of impurities by distillation in steam, the product solidified, and then crystallised from alcohol in beautiful colourless plates, m. p. 90°, b. p. 250°/3 mm. (Found: C, 67·9; H, 5·04; Sn, 26·5. $C_{25}H_{22}Sn$ requires C, 68·1; H, 5·0; Sn, 27·0%). The substance is readily soluble in the usual solvents with the exception of alcohol.

Phenylbenzylstannic Chloride.—Triphenylbenzylstannane (1 mol.) in chloroform was treated with iodine (1 mol.), which was added gradually as the colour was discharged. After removal of the solvent and iodobenzene by distillation either in steam or under diminished pressure, an oil remained which could not be obtained crystalline. It was therefore treated with ammonia, and the resultant hydroxide warmed with dilute hydrochloric acid. On cooling, a solid was produced which crystallised from petroleum (b. p. 80—100°) in colourless needles, m. p. 83—84° (Found: C, 43·98; H, 3·4; Cl, 19·6. $C_{13}H_{12}SnCl_2$ requires C, 43·6; H, 3·4; Cl, 19·8%). Here, apparently, the gentle warming with hydro-

chloric acid has been sufficient to remove one of the phenyl groups from the molecule. *Phenylbenzylstannic chloride* was also produced by warming triphenylbenzylstannane with concentrated hydrochloric acid for a few minutes—prolonged boiling results in the complete breakdown of the molecule, stannous chloride being formed.

Tribenzyl-p-tolylstannane was prepared from tribenzylstannic chloride and *p*-tolyl magnesium bromide in the usual way. It does ; solidify at 0°, and treatment with iodine or hydrochloric acid ults in the formation of tribenzylstannic iodide or chloride ectively.

Triphenyl-*p*-tolylstannane (*Ber.*, 1919, **52**, 2150), on treatment with iodine and conversion of the iodide into chloride, yielded triphenylstannic chloride.

Triphenyl-o-tolylstannane, from triphenylstannic iodide and *o*-tolyl magnesium bromide, crystallised easily from diacetone-alcohol or petroleum in stout, colourless needles, m. p. 165° (Found: C, 67·6; H, 5·4; Sn, 26·7. $C_{25}H_{22}Sn$ requires C, 68·1; H, 5·0; Sn, 27·0%). Treatment with iodine resulted in the formation of o-iodotoluene and triphenylstannic iodide. Boiling with hydrochloric acid for a few seconds similarly gave toluene and triphenylstannic chloride.

Tetra-*p*-tolylstannane (*Z. anorg. Chem.*, 1910, **68**, 122) on treatment with 1 mol. of iodine in choroform yielded tri-*p*-tolylstannic iodide (*Ber.*, 1920, **53**, 183). Boiling hydrochloric acid converted tetra-*p*-tolylstannane into an oil which was extracted with petroleum; after prolonged standing, crystals, m. p. 38—40°, were formed, which were doubtless di-*p*-tolylstannic chloride (J., 1913, **103**, 2049).

Tri-p-tolyl-o-tolylstannane, prepared as usual from tri-*p*-tolylstannic chloride and *o*-tolyl magnesium bromide, crystallised readily from petroleum in colourless prisms, m. p. 168° (Found: Sn, 24·5, 24·65. $C_{28}H_{28}Sn$ requires Sn, 24·65%). It is readily soluble in benzene and chloroform, fairly so in hot acetone, and not very readily in alcohol. Treatment with iodine results in the formation of *o*-iodotoluene and tri-*p*-tolylstannic iodide.

Tri-m-tolylstannic Chloride.—Treatment of tetra-*m*-tolylstannane (*Ber.*, 1920, **53**, 184) with 1 mol. of iodine resulted in the production of an oily iodide which was decomposed with ammonia and then treated with dilute hydrochloric acid; the *chloride* crystallised easily from alcohol or petroleum in small, colourless prisms, m. p. 108—109° (Found: Cl, 8·2. $C_{21}H_{21}SnCl$ requires Cl, 8·3%).

Tri-m-tolyl-p-tolylstannane, from tri-*m*-tolylstannic chloride and *p*-tolylmagnesium bromide, crystallised from alcohol in minute, colourless needles, m. p. 103° (Found: Sn, 24·8. $C_{28}H_{28}Sn$ requires Sn 24·65%). Treatment with iodine resulted in the formation of an

iodide which could not be obtained pure and was probably a mixture of tri-*m*-tolylstannic and di-*m*-tolyl-*p*-tolylstannic iodides. The iodotoluene evolved would not solidify and was probably a mixture of the *o*- and *p*-isomerides.

*Phenyldi-*p*-tolylbenzylstannane* was prepared by addition of phenylbenzylstannic chloride to excess of *p*-tolyl magnesium bromide; it has b. p. 265—270°/2—3 mm. and does not solidify (Found: C, 69·2; H, 5·6. $C_{27}H_{26}Sn$ requires C, 69·1; H, 5·55%). It is readily soluble in the usual solvents with the exception of methyl and ethyl alcohols. Treatment with boiling hydrochloric acid resulted in the expulsion of the two tolyl groups and formation of phenylbenzylstannic chloride.

*Phenyl-*p*-tolylbenzylstannic Hydroxide.*—Attempts to prepare salts of this base by treatment of phenylbenzylstannic chloride with 1 mol. of *p*-tolyl magnesium bromide resulted in failure, phenyldi-*p*-tolylbenzylstannane being formed and some of the halide remaining unattacked; but treatment of phenyldi-*p*-tolylbenzylstannane in chloroform solution with 1 mol. of iodine resulted in elimination of *p*-iodotoluene and formation of an oily *iodide*. This salt was therefore treated with ammonia and a solid *hydroxide* produced, which after three crystallisations from ethyl acetate melted at 136—137° (Found: C, 60·98; H, 5·14; Sn, 30·1. $C_{20}H_{20}OSn$ requires C, 60·8; H, 5·07; Sn, 30·1%). The d-*camphorsulphonate* of this base was obtained by dissolving equimolecular proportions of it and the acid in acetone. Evaporation of the solvent left an oil which resisted all attempts at crystallisation. It was readily soluble in acetone, alcohol, ethyl acetate, and chloroform, but almost insoluble in water and petroleum. Solution in acetone followed by precipitation by water was carried out six times, but the product was still oily, and the base recovered from the salt optically inactive. The d-*α-bromo-π-camphorsulphonate*, prepared by dissolving the base in an equivalent quantity of the acid in alcoholic solution, was also oily; it is readily soluble in ether, sparingly so in alcohol, and almost insoluble in water. After fractional precipitation of an acetone solution by addition of water, the salt still resisted crystallisation, and the base recovered from it was optically inactive. The d-*tartrate* was an amorphous solid almost insoluble in the usual solvents, with the exception of alcohol; fractional precipitation of an alcoholic solution by addition of petroleum produced no change in the properties of the salt and the recovered base was optically inactive.

*Triphenyl-*n*-butylstannane*, prepared in the usual manner from triphenylstannic iodide and *n*-butyl magnesium bromide, crystallises readily from hot alcohol in colourless needles, m. p. 61—62°, b. p.

222°/3 mm. (Found: Sn, 28·9; 29·7. $C_{22}H_{24}Sn$ requires Sn. 29·3%), and is readily soluble in petroleum, ethyl acetate, and benzene. Boiling with hydrochloric acid for a few seconds converts this compound into *phenyl*-n-*butylstannic chloride*, crystallising from light petroleum (b. p. 40—60°) in colourless prisms, m. p. 50° (Found: C, 37·12; H, 4·39; Cl, 21·4. $C_{10}H_{14}SnCl_2$ requires C, 37·0; H, 4·32; Cl, 21·9%).

Diphenylbenzyl-n-*butylstannane*.—Triphenylbenzylstannane (1 mol.) in chloroform was treated with iodine (1 mol.), and after completion of the reaction, the solvent and iodobenzene were removed by distillation under reduced pressure. To the oily *iodide* produced in this manner was added an ethereal solution of *n*-butyl magnesium bromide (1½ mols.); the product was worked up as usual and a colourless oil isolated, b. p. 215°/2—3 mm. (Found: Sn, 28·5, 28·3. $C_{23}H_{26}Sn$ requires Sn, 28·3%). This compound was also prepared by treatment of triphenylbutylstannane successively with iodine and benzyl magnesium chloride.

Phenylbenzyl-n-*butylstannic Hydroxide*.—Diphenylbenzylbutylstannane was treated with 1 mol. of iodine in chloroform solution, and the solvent evaporated. Distillation of the residue under reduced pressure yielded an iodide, b. p. 185—189°, which was clearly iodobenzene, and left an oil which was converted into a solid *hydroxide* by treatment with ammonia; crystallisation twice from benzene and then twice from alcohol gave a product, m. p. 135—137° (not sharp) (Found: Sn, 33·0. $C_{17}H_{22}OSn$ requires Sn, 33·0%). Although the chloride, bromide, and iodide of this base were oils, a crystalline *fluoride* was precipitated by addition of an aqueous solution of neutral potassium fluoride to the base dissolved in alcohol and acetic acid; the product crystallised from alcohol in colourless needles, m. p. 218° (Found: C, 56·3; H, 5·9. $C_{17}H_{21}SnF$ requires C, 56·3; H, 5·8%).

The d-*camphorsulphonate* of phenylbenzyl-*n*-butylstannic hydroxide was formed both by dissolution of the base in an acetone solution of the acid and by double decomposition of the iodide with silver *d*-camphorsulphonate. The salt could not, however, be obtained solid even after fractional precipitation of an acetone solution with water; the d-*α-bromo-π-camphorsulphonate* and the d-*camphorate* were also persistently oily. The d-*tartrate* was an amorphous solid which did not melt at 250°, but melted under hot alcohol; it was dissolved in this solvent and allowed to separate again several times, and the alcoholic solution was then precipitated with aqueous potassium fluoride, but the fluoride so formed was optically inactive in alcoholic solution.

Tribenzylethylstannane is decomposed by iodine with the elimin-

ation of one of the benzyl groups (J., 1912, **101**, 2553). On the other hand, it was found that hydrochloric acid acts on this substance only with extreme slowness, and after an hour's heating under reflux a solid product was obtained which proved to be tribenzylstannic chloride.

*Dibenzylethyl-*n*-butylstannane*, prepared from tribenzylethylstannane in an exactly similar manner to the preparation of diphenylbenzyl-*n*-butyl- from triphenylbenzyl-stannane, is a colourless oil, b. p. 195—200°/3—5 mm. (Found : C, 61·6; H, 7·5. $C_{20}H_{28}Sn$ requires C, 62·0; H, 7·3%).

*Salts of Benzylethyl-*n*-butylstannic Hydroxide.*—Treatment of dibenzylethyl-*n*-butylstannane with 1 mol. of iodine gave an oily *iodide* which was dissolved in alcohol and treated with one equivalent of silver *d*-camphorsulphonate in water; the silver iodide was removed by filtration and the filtrate evaporated, but the resulting oil could not be crystallised. Similar results were obtained by using silver *d*-α-bromo-π-camphorsulphonate.

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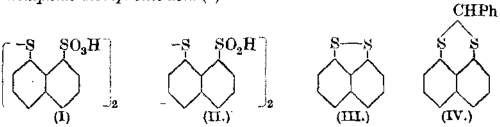
CCCXIII.—*Naphthylene* 1 : 8-*Disulphide.*

By WILLIAM BENNETT PRICE and SAMUEL SMILES.

THE experiments which have been made on the formation of sulphur ring systems (J., 1922, **121**, 87; 1926, 1821, 2265; 1927, 534; this vol., pp. 697, 1142) have now been extended to the inclusion of the *peri*-system of naphthalene in five- and six-membered dithioring systems.

1-Naphthylamine-8-sulphonic acid was found to be the most convenient source of the required 1 : 8-dithiolnaphthalene. When naphthalene-1 : 8-diazosulphonate was treated with sulphurous acid in presence of copper the 1 : 8-*sulphino-sulphonic acid* was obtained, and reduction of this acid in aqueous solution with sulphurous acid and dilute hydriodic acid gave a good yield of the corresponding *disulphide-disulphonic acid* (I).



(I) (II.) (III.) (IV.)

Treatment of the chloride of this acid in the usual way gave 1 : 1′-*dithiodinaphthalene*-8 : 8′-*disulphinic acid* (II), which finally was

reduced to the required 1 : 8-*dithiolnaphthalene*. This unstable mercaptan on exposure to air or in solution with mild oxidising agents yielded the orange *disulphide* (III), whilst the simultaneous formation of complex polysulphides was not observed. The ease with which this cyclic system is formed at the *peri*-position of naphthalene accords with the existence of the corresponding sultone and sultan, and also with the stability of *o*-dithiobenzoyl and of diphenyl 2 : 2′-disulphide and -disulphoxide. A further resemblance between the behaviour of 2 : 2′-dithioldiphenyl and that of 1 : 8-dithiolnaphthalene is found in the action of the latter with aldehydes, which furnish the six-membered system in the mercaptals (IV). The results of these experiments amplify the evidence now available from numerous sources of the stability of five- and six-membered dithio-ring systems.

EXPERIMENTAL.

1-*Sulphinonaphthalene*-8-*sulphonic Acid*.—A mixture of water (250 c.c.) and the diazosulphonate prepared from 50 g. of 1-naphthylamine-8-sulphonic acid was saturated with sulphur dioxide. After treatment with copper powder in the usual manner, the liquid was warmed and passed through a filter (2 g. of charcoal). When the clear liquid was saturated with salt, the *sodium* salt of the required sulphonic acid separated. A sample was purified from hot water (Found : S, 22·3. $C_{10}H_7O_5S_2Na$ requires S, 21·77%).

1 : 1′-*Dithiodinaphthalene*-8 : 8′-*disulphonic Acid* (I).—An aqueous solution (400 c.c.) of the mono-sodium salt obtained from the foregoing process, containing hydrogen iodide (3 or 4 drops, *d* 1·7), was kept at 95—100° for 3 hours and treated with a slow current of sulphur dioxide. After the clear liquid had been concentrated and cooled, the *sodium* salt of the required acid separated in flocculent aggregates, and was purified from hot water (Found : Na, 9·0. $C_{20}H_{12}O_6S_4Na_2$ requires Na, 8·8%).

1 : 1′-*Dithiodinaphthalene*-8 : 8′-*disulphinic Acid* (II).—The dried sodium sulphonate thus obtained was triturated (10 g.) with phosphorus pentachloride (20 g.). The mixture was kept for 6 hours, the crude sulphonic chloride being then isolated in the usual manner. The use of larger quantities of material and higher temperatures gave less favourable results. The crude acid chloride was treated for 10 minutes with a boiling aqueous solution of an equal weight of sodium sulphite. When the cooled and clear solution (charcoal) was mixed with sulphuric acid, the required *sulphinic acid* separated in needles, which when purified from alcohol had m. p. 144° (Found : C, 53·7 ; H, 3·0. $C_{20}H_{14}O_4S_4$ requires C, 53·8 ; H, 3·1%).

1 : 8-*Dithiolnaphthalene*.—Zinc dust (4·5 g.) was gradually added

to the warm mixture of the sulphinic acid (1 g.) with alcohol (15 c.c.) and concentrated hydrochloric acid (15 c.c.). After the reaction had been maintained for 2 hours, the required mercaptan separated from the cooled liquid in colourless plates; these had m. p. 113—114° and were readily soluble in common organic solvents, but attempts further to purify the substance were abandoned owing to the ease with which it is converted into the disulphide. The substance was characterised as the dimethylthiol which was obtained by treatment with methyl sulphate in presence of aqueous alkali. 1 : 8-*Dimethyldithiolnaphthalene* formed colourless plates, m. p. 84°, from acetic acid (Found: C, 65·3; H, 5·5. $C_{12}H_{12}S_2$ requires C, 65·4; H, 5·4%).

When alcoholic solutions of the dithiol and nickel acetate are mixed, a characteristic *nickel* derivative is precipitated in the crystalline state. This brownish-purple substance (Found: Ni, 23·5. $C_{10}H_6S_2Ni$ requires Ni, 23·7%) is slightly soluble in chloroform; it appears to contain the co-ordinated metal but its constitution has not been examined.

2-*Phenyl*-peri-*naphtha*-1 : 3-*dithiane* (IV).—1 : 1′-Dithiodinaphthalene-8 : 8′-disulphinic acid was reduced with zinc dust and alcohol into which dry hydrogen chloride was passed. When reduction was complete, the requisite amount of benzaldehyde was added to the solution, which was then saturated with hydrogen chloride. After being kept for 12 hours, the solution was mixed with water and the required material then separated in the crystalline state. It was purified from aqueous alcohol and formed needles, m. p. 116° (Found: C, 73·1; H, 4·7. $C_{17}H_{12}S_2$ requires C, 72·85; H, 4·3%).

Naphthylene 1 : 8-*Disulphide* (III).—This is readily obtained by spontaneous oxidation of the dithiol in presence of atmospheric oxygen. It was prepared by passing air through a solution of the dithiol in ammonia. The precipitated material was purified from alcohol and formed orange plates, m. p. 116° (Found: C, 62·8; H, 4·3; *M*, 191. $C_{10}H_6S_2$ requires C, 63·1; H, 3·1%; *M*, 190). In the preparation of this disulphide, the use of ferric chloride should be avoided owing to the formation of complex iron derivatives of the mercaptan which contaminate the product. Oxidation of the disulphide readily ensues in presence of hydrogen peroxide in acetic acid; a study of the process has shown that it proceeds beyond the thiolsulphonate and that successive oxidation products are generally formed simultaneously. The separation of these was not satisfactorily accomplished with the amount of material available.

KING'S COLLEGE, LONDON. [*Received, July* 11*th*, 1928.]

CCCXIV.—*Certain Aryl Arsenoxides and the Corresponding Dichloro- and Di-iodo-arsines.*

By George Newbery and Montague Alexandra Phillips.

In the course of chemo-therapeutic studies proceeding in these laboratories, a number of dichloro- and di-iodo-arsines and the corresponding arsenoxides were prepared, and some of their chemical properties are now recorded. Some phenyl-arsine derivatives, prepared for comparison, are also described.

In general, the dihalogeno-arsines are hydrolysed by water to give the corresponding arsenoxides, and can be regenerated by the action of the halogen acid. The hydrolysis is obvious in cases such as those of 3 : 5-*diacetamido*-2- and -4-*hydroxyphenyldichloroarsines*, where the product of hydrolysis is insoluble in the concentration of mineral acid simultaneously formed (compare the dicyano-arsines, Grischkievitsch-Trochimovski, Mateyak, and Zablotski, *Bull. Soc. chim.*, 1927, **41**, 1323). The amino-di-iodoarsine hydriodides are much less soluble in water than the corresponding chloro-derivatives, from which they can readily be made by addition of hydriodic acid or potassium iodide in aqueous solution. In general, the attachment of the iodine atom to the arsenic atom appears to be firmer than that of the chlorine atom in the corresponding chloro-compound; this stability extends to concentrated nitric acid, and in one case, *viz.*, 3 : 5-*diamino*-4-*hydroxyphenyldi-iodoarsine dihydriodide*, even to 5*N*-sodium hydroxide solution. The di-iodo-arsines are deep yellow, crystalline compounds, whereas the pure chloro-compounds are white.

It is noteworthy that 3 : 5-*diacetamido*-4-*hydroxyphenylarsenoxide*, made either by hydrolysis of the dichloro-arsine or by acetylation of 3-*amino*-5-*acetamido*-4-*hydroxyphenylarsenoxide*, appears to exist only as the arsinous acid, which does not lose water at 100°. In this way it differs from the "arsenoxide hydrates" of Lewis and Cheetham (*J. Amer. Chem. Soc.*, 1921, **43**, 2119) and from 3 : 5-*diacetamido*-2-*hydroxyphenylarsenoxide*, although it resembles the latter in its ready solubility in ammonium hydroxide and sodium carbonate solutions (compare also benzarsenious acid, La Coste, *Annalen*, 1881, **208**, 14).

Attention must also be directed to a curious property of 3-*amino*-5-*acetamido*-2- and -4-*hydroxyphenylarsenoxide hydrochlorides* and *hydriodides*. These four compounds will only dissolve in water after standing for a few seconds, and it is possible that they may actually be the free bases corresponding to chloro-hydroxy-arsines of the type $C_6H_2(NH_2)(OH)(NHAc)\cdot As(OH)Cl$, hydrolysed by water

to give $C_6H_2(NH_2,HCl)(OH)(NHAc)\cdot AsO$. *Addition of* hydrochloric acid to the alkaline solutions until they are acid to Congo-red precipitates the original compounds with their characteristic delayed solubility in water.

In attempts to prepare compounds of the type As(OH)ClR by the action of methyl-alcoholic hydrogen chloride on the corresponding arsenoxide, *methoxy-3-acetamido-4-hydroxy-* and *-5-acetamido-2-hydroxy-phenylchloroarsines* were obtained. These compounds *gave the corresponding arsenoxides* on treatment with water.

Experimental.

3-Nitro-5-acetamido-2-hydroxyphenylarsinic Acid.—This compound was obtained by dissolving 100 g. of 5-acetamido-2-hydroxyphenylarsinic acid (Newbery and Phillips, this vol., p. 116) in sulphuric acid (300 c.c.) at 20°, nitrating it at 10—20° with a mixture of nitric acid (*d* 1·420; 35 c.c.) and sulphuric acid (35 c.c.), and pouring into ice water; the *pure nitro-compound* separated in 80% yield as yellow prisms, giving red solutions in caustic alkalis and alkali carbonates (Found: As, 23·5. $C_8H_9O_7N_2As$ requires As, 23·4%).

3-Amino-5-acetamido-4- and *-2-hydroxyphenylarsinic acids* were obtained by reduction of the corresponding nitro-acids (compare Jacobs, Heidelberger, and Rolf, *J. Amer. Chem. Soc.*, 1918, **40**, 1580; 60% yield in each case), and purified by the method described by Christiansen (*ibid.*, 1920, **42**, 2403) for 3-amino-4-hydroxyphenylarsinic acid. The former consists of stout white prisms, readily soluble in dilute mineral acids, and in alkali hydroxides and carbonates (Found: As, 25·6; N, 9·3. $C_8H_{11}O_5N_2As$ requires As, 25·8; N, 9·7%), whilst the isomeric acid (Found: As, 25·8; N, 9·6%) is only soluble in excess of dilute mineral acids.

3:5-*Diacetamido-2-hydroxyphenylarsinic acid* and 3:5-diacetamido-4-hydroxyphenylarsinic acid, the latter of which has been described by Raiziss and Gavron (*ibid.*, 1921, **43**, 584), were best made by the following method: 3-Nitro-5-acetamido-2- or -4-hydroxyphenylarsinic acid (30 g.) was dissolved in 2*N*-sodium hydroxide, and sodium hyposulphite (54 g.) was slowly added at 10° with stirring. After 30 minutes, 10*N*-sodium hydroxide was added, the solution filtered, and acetic anhydride (30 c.c.) run in. After 1 hour the reaction mixture was acidified (Congo-red), and the precipitated arsinic acid purified through its alkaline solution. The yield varied from 10 to 15 g. in each case. The 2-hydroxy-acid forms white needles, readily soluble in alkalis (Found: As, 22·6; N, 8·3. $C_{10}H_{13}O_6N_2As$ requires As, 22·6; N, 8·4%), and its orientation is shown by its conversion into 2:4-diaminophenol (isolated as diacetyl derivative) by boiling with 5 parts of 15% hydrochloric acid.

The aminophenyldichloroarsines were prepared by sulphurous acid reduction of the arsinic acid in hydrochloric acid at room temperature, a trace of potassium iodide being present; some acetamido-derivatives were made by addition of a warm solution of the corresponding arsinic acid in hydrochloric acid to a solution of sulphurous acid containing potassium iodide, and passage of sulphur dioxide at 10° until reduction was complete. The dichloro-arsine was precipitated where necessary by addition of a sufficient amount of concentrated hydrochloric acid. The aminodi-iodoarsine hydriodides were similarly prepared by use of either an acidified solution of potassium iodide or hydriodic acid.

3-Amino-5-acetamido-4-hydroxyphenylarsine Derivatives.—The *dichloro-arsine hydrochloride*, obtained in 60% yield by the general method, formed white prisms, soluble in dilute alkali hydroxide (Found: As, 21·5; N, 8·0; Cl, 30·5. $C_8H_9O_2N_2Cl_2As,HCl$ requires As, 21·6; N, 8·05; Cl, 30·6%). This hydrochloride (5 g.) was suspended in water (30 c.c.) and stirred for 30 minutes; the resulting amorphous solid was collected, washed with water, and crystallised by addition of concentrated hydrochloric acid to the solution in sodium hydroxide until faintly acid to Congo-red (yield, 2·3 g.). *3-Amino-5-acetamido-4-hydroxyphenylarsenoxide hydrochloride* thus obtained formed white prisms, soluble in water after a few seconds' shaking, and readily soluble in dilute caustic alkalis (Found: As, 25·6; N, 9·7; Cl, 12·2. $C_8H_9O_3N_2As,HCl$ requires As, 25·6; N, 9·6; Cl, 12·1%).

The amorphous arsenoxide, obtained as described above from 2 g. of dichloro-arsine hydrochloride, was collected, washed with water, and stirred into a mixture of hydriodic acid (*d* 1·7; 40 c.c.) and water (20 c.c.); the gum formed soon crystallised as prisms and was found to be pure *3-amino-5-acetamido-4-hydroxyphenyldi-iodoarsine hydriodide* (Found: As, 11·9; N, 4·4; I, 61·9. $C_8H_9O_2N_2I_2As,HI$ requires As, 12·0; N, 4·5; I, 61·2%). This compound was also obtained by the general method; its acetyl group is remarkably stable to hot mineral acids, and it readily dissolves in water to give a yellow solution which deposits crystals of the arsenoxide. *3-Amino-5-acetamido-4-hydroxyphenylarsenoxide hydriodide* forms white prisms, soluble in water only after a few seconds' shaking (Found: As, 19·7; I, 32·6. $C_8H_9O_3N_2As,HI$ requires As, 19·5; I, 33·0%).

3 : 5-*Diamino-4-hydroxyphenyldichloroarsine dihydrochloride.* The above dichloro-arsine hydrochloride (30 g.) was boiled for 15 minutes with 120 c.c. of 5*N*-hydrochloric acid, and sufficient hot water to dissolve the solid was then added. Addition of an equal volume of concentrated hydrochloric acid to the hot filtered solution gave, on

cooling, a 50% yield of the required *dihydrochloride* as white plates, readily soluble in water (Found: As, 21·7; N, 8·1; Cl, 41·0. $C_6H_7ON_2Cl_2As,2HCl$ requires As, 21·9; N, 8·1; Cl, 41·5%).

To this chloro-compound (5 g.) in water (50 c.c.), hydriodic acid (*d* 1·7: 30 c.c.) was added; the solid was collected, washed with alcohol and ether, and dried in a vacuum over caustic soda and calcium chloride, 3 : 5-*diamino-4-hydroxyphenyldi-iodoarsine dihydriodide* being thus obtained as yellow prisms, readily soluble in water (yield, 7 g.) (Found: As, 10·7; I, 72·0. $C_6H_7O_2N_2I_2As,2HI$ requires As, 10·1; I, 72·0%).

3-*Amino-5-acetamido-2-hydroxyphenylarsine Derivatives*.—The *di-iodoarsine hydriodide* was obtained by the general method as yellow, boat-shaped crystals (Found: As. 11·9; N, 4·6; I, 62·1%), soluble in water to give a yellow solution, which slowly deposits crystals of the oxide hydriodide.

The *arsenoxide hydriodide* forms white prisms, soluble in water only after shaking for a few seconds (Found: As, 19·6; I, 33·0%).

3 : 5-*Diacetamido-2- and -4-hydroxyphenyldichloroarsines*.—These were obtained by the general method, or by the action of alcoholic hydrogen chloride on the corresponding arsenoxide, as clusters of needles readily soluble in water, by which they were slowly hydrolysed. They could not be obtained sufficiently pure for analysis.

3 : 5-*Diacetamido-4-hydroxyphenylarsinous acid* was obtained (1) by hydrolysis of the dichloro-arsine; (2) by acetylation of 3-amino-5-acetamido-4-hydroxyphenyldichloroarsine hydrochloride as described under 5-acetamido-2-hydroxyphenylarsenoxide (see below); or (3) by acetylation of 3 : 5-diamino-4-hydroxyphenyldichloroarsine dihydrochloride. It was purified by solution in caustic alkali and acidification by hydrochloric acid (Congo-red), and consisted of white plates or needles, insoluble in water, dilute mineral acids, or sodium bicarbonate solution, but soluble in aqueous solutions of sodium hydroxide, sodium carbonate, or dilute ammonia (Found: As, 23·8; N, 8·9. $C_{10}H_{13}O_5N_2As$ requires As, 23·7; N, 8·9%).

3 : 5-*Diacetamido-2-hydroxyphenylarsenoxide*, obtained by aqueous hydrolysis of the corresponding dichloro-arsine, is an amorphous, white solid with solubilities identical with the above arsenious acid. It was purified similarly, and dried at 100° (Found: As, 24·8; N, 9·4. $C_{10}H_{11}O_4N_2As$ requires As, 25·1; N, 9·4%).

Derivatives of 3-Amino-4-hydroxyphenylarsine.—The dichloroarsine was obtained by the general method as a monohydrate. On treatment of its aqueous solution with excess of hydriodic acid, it gave the corresponding *di-iodoarsine hydriodide*, which was also obtained by the general method: this formed yellow prisms, giving a yellow solution in water. The iodine attached to the arsenic atom

showed some resistance to the action of hot 8*N*-nitric acid, only one-third of the total iodine being removed (Found: As, 13·5; I, removed by concentrated nitric acid, 68·0. $C_6H_6ONI_2As,HI$ requires As, 13·3; I, 67·5%).

The hydrolysis of the dichloro-arsine hydrochloride was accomplished by dissolution in water (3 g. in 10 c.c.); the solution deposited the crude oxide hydrochloride, whilst the filtrate contained approximately two-thirds of the total chlorine introduced.

3-Acetamido-4-hydroxyphenylarsenoxide. This compound was obtained by the methods since given in E.P. 254,186 and F.P. 606,238, but is best obtained as follows: To 3-amino-4-hydroxyphenyldichloroarsine (25 g.), dissolved in water (80 c.c.), acetic anhydride (37·5 c.c.) is added, followed at once by sodium acetate until the mixture no longer reacts acid to Congo-red. After acidification (Congo-red) by 25% sulphuric acid, the crude acetyl derivative is collected and washed. The *oxide*, purified by acidification of its solution in sodium hydroxide by 25% sulphuric acid, forms a tetrahydrate consisting of white prisms, which lose water at 100°. It is insoluble in water, sodium bicarbonate, or sodium carbonate solution, but soluble in excess of caustic alkalis and in large excess of ammonia (Found: H_2O lost at 100°, 23·1. Calc.: H_2O, 23·0. Found, in dried material: As, 30·9; N, 5·7. Calc.: As, 31·1; N, 5·8%).

Derivatives of 5-Amino-2-hydroxyphenylarsine.—Sulphur dioxide was passed for 90 minutes through a solution of 20 g. of 5-amino-2-hydroxyphenylarsinic acid in water (60 c.c.) and hydrochloric acid (200 c.c.). The precipitated *5-amino-2-hydroxyphenyldichloroarsine hydrochloride*, purified by solution in water (80 c.c.) and reprecipitation by 160 c.c. of hydrochloric acid (yield, 15·5 g.), consisted of anhydrous, white prisms, soluble in four parts of water (Found: As, 25·5; N, 4·8; Cl, 37·0. $C_6H_6ONCl_2As,HCl$ requires As, 25·7; N, 4·8; Cl, 36·8%); the basified solution is much more stable to aerial oxidation than that of its isomeride.

5-Amino-2-hydroxyphenylarsenoxide hydrochloride, white prisms soluble in water, was obtained by dissolving the above dichloroarsine hydrochloride (2 g.) in water (8 c.c.) and collecting the crystals which separated after some hours (Found: As, 31·5; Cl, 15·1. $C_6H_6O_2NAs,HCl$ requires As, 31·9; Cl, 15·1%).

5-Amino-2-hydroxyphenyldi-iodoarsine hydriodide, made by the general methods, consisted of yellow prisms, soluble in water to give a yellow solution (Found: As, 13·5; N, 2·7. I, removed by hot 8*N*-nitric acid, 22·8; I, removed by concentrated nitric acid, 67·7. $C_6H_6ONI_2As,HI$ requires As, 13·3; N, 2·5; I, 67·5%).

5-Amino-2-hydroxyphenylarsenoxide hydriodide was obtained as

stout, white prisms, by shaking the above di-iodoarsine hydriodide (1 g.) with water (10 c.c.); it resembles its isomeride in properties and solubilities (Found: As, 22·7; I, 40·0. $C_6H_6O_2NAs,HI$ requires As, 22·9; I, 38·9%).

5-Acetamido-2-hydroxyphenylarsenoxide was best prepared by dissolving the corresponding aminodichloroarsine hydrochloride (15 g.) in water (50 c.c.), cooling during addition of acetic anhydride (25 c.c.), and adding sodium acetate. The acetyl compound which separated was purified as in the case of its isomeride, and formed white anhydrous prisms having similar solubilities (Found: As, 31·3; N, 5·7. $C_8H_8O_3NAs$ requires As, 31·1; N, 5·8%).

3-Acetamido-4-hydroxy- and 5-Acetamido-2-hydroxy-phenyldichloroarsines.—These derivatives were obtained by trituration of the corresponding arsenoxide with excess of alcoholic hydrogen chloride. On spontaneous evaporation, crystals of the dichloro-arsine were obtained, which were purified by solution in alcohol and precipitation by ether. They formed white or pale yellow needles, soluble in cold alcohol and in cold water: the latter hydrolysed them slowly to give the corresponding arsenoxide (Found, for *3-acetamido-4-hydroxyphenyldichloroarsine*: As, 25·1; N, 4·7; Cl, 24·1; for *5-acetamido-2-hydroxyphenyldichloroarsine*: As, 25·1; N, 4·8; Cl, 24·0. $C_8H_8O_2NCl_2As$ requires As, 25·1; N, 4·75; Cl, 24·0%).

3-Nitro-4-hydroxy-5-aminophenyldi-iodoarsine hydriodide, made from the corresponding arsinic acid (compare Fourneau, *loc. cit.*) by the general method, consisted of yellow prisms, dissolving in water to give a yellow and in alkali carbonate or hydroxide to give red solutions (Found: As, 12·1; N, 5·0; I, 58·5. $C_6H_5O_3N_2I_2As$ requires As, 12·3; N, 4·6; I, 62·4%). On acetylation in alkaline solution, it gave *3-nitro-4-hydroxy-5-acetamidophenylarsenoxide*, an amorphous, white solid, insoluble in water and giving deep red solutions with caustic alkalis (Found: As, 25·8. $C_8H_7O_5N_2As$ requires As, 26·2%).

3-Acetamido-4-hydroxy- and 5-Acetamido-2-hydroxy-phenylmethoxychloroarsines.—To the corresponding arsenoxide (4·8 g.), dissolved at room temperature in methyl alcohol (90 c.c.), 15% methyl-alcoholic hydrogen chloride (2·4 c.c.) was added, the solution kept for 30 mins., and concentrated under reduced pressure to 10 c.c.; the methoxychloro-compound then crystallised out (yield, 70% in each case). *3-Acetamido-4-hydroxyphenylmethoxychloroarsine* (Found: As, 25·8; N, 4·8; Cl, 12·2%) and *5-acetamido-2-hydroxyphenylmethoxychloroarsine* (Found: As, 25·7; N, 5·0; Cl, 12·2; MeO, 10·3. $C_9H_{11}O_3NClAs$ requires As, 25·7; N, 4·8; Cl, 12·2; MeO, 10·6%) each consisted of white prisms, readily converted by warm water into the corresponding arsenoxide.

3-*Acetamido-4-hydroxyphenylarsine*.—A mixture of 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene (5 g.) and zinc dust (16 g.) was added to concentrated hydrochloric acid (70 c.c.) and water (50 c.c.) at 90—100°; after cooling, the clear supernatant liquid was filtered into a solution of sodium acetate (20 g.) in water (20 c.c.) containing acetic anhydride (15 c.c.) in suspension. On shaking, 3-*acetamido-4-hydroxyphenylarsine* separated in 90% yield (Found: As, 33·0; N, 6·3. $C_8H_{10}O_2NAs$ requires As, 33·0; N, 6·2%); *it formed white plates, insoluble in water but soluble in excess of caustic alkalis.*

5-*Acetamido-2-hydroxyphenylarsine*, similarly prepared from the corresponding arsenobenzene, also forms white plates (Found: As, 32·8; N, 6·3%). Both arsines are readily oxidised by air to the corresponding arseno-compound.

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CCCXV.—*The Apparent Hydration of Ions. Part II. The Densities and Viscosities of some Mixed Aqueous Solutions of Lithium Chloride and Hydrochloric Acid.*

By JOHN WILLIAM INGHAM.

THE methods described in Part I (this vol., p. 1917) for the investigation of the hydration of potassium and sodium chlorides in concentrated aqueous solutions containing hydrochloric acid have now been applied to certain mixed solutions of lithium chloride and hydrochloric acid. The densities and viscosities at 25° have been determined for a series of solutions containing different proportions of the acid and the salt with approximately the same total solute concentration as a saturated solution of sodium chloride, such a concentration being chosen so that a direct comparison might be made of the behaviour of the two salts under similar conditions.

The experimental work was carried out in the same way as for Part I, but, since the solutions were not saturated, they were made by mixing stock solutions of known concentration. The opportunity was taken of further testing the Scarpa method for measuring the viscosities by carrying out determinations in an Ostwald tube upon the same solutions. The same viscometers were used as for Part I. The results confirmed the previous conclusions as to the accuracy of the Scarpa method. In Table I, col. I shows the densities calculated from the formula

$$d_{4^\circ}^{25^\circ} = 0{\cdot}99707\,W'/W - 0{\cdot}0012(W' - W)/W;$$

cols. 2 and 3 the coefficients of viscosity in c.g.s. units; cols. 4, 5, and 6 the concentrations (mols./litre) of acid, salt, and water, respectively; and col. 7 the hydration numbers, x. The total *solute concentrations varied between 5·459 and 5·402, that previously* found for saturated sodium chloride solution at 25° being 5·4325.

TABLE I.

$d_{4°}^{25°}$.	η (Scarpa).	η (Ostwald).	HCl.	LiCl.	H_2O.	x.
1·1176	0·01951	0·01944	0	5·407	49·20	2·49
1·1147	0·01849	0·01839	0·546	4·913	49·20	2·36
1·1116	0·01748	0·01746	1·091	4·364	49·20	1·81
1·1087	0·01667	0·01664	1·635	3·799	49·29	2·12
1·1050	0·01581	0·01579	2·176	3·248	49·29	1·91
1·1019	0·01509	0·01508	2·702	2·708	49·34	1·89
1·0985	0·01440	0·01435	3·246	2·160	49·32	1·72
1·0957	0·01384	0·01384	3·789	1·635	49·30	1·82
1·0920	0·01320	0·01318	4·330	1·072	49·34	1·80
1·0893	0·01267	0·01263	4·890	0·540	49·29	

Except in the case of the first two solutions, the agreement between the viscosities obtained by the different methods was good. The viscosity of the stock lithium chloride solution (5·407*M*) as found by the Scarpa method was in better agreement with Green's data for that salt (J., 1908, **93**, 2023) than was the value given by the Ostwald method. Any errors in density determinations are reflected in the latter method and do not affect the Scarpa values.

Discussion of Results.

Densities and Solution Volumes.—It is found that, although the densities can be calculated by means of the formula $d_{4°}^{25°} = K + k_1a + k_2b$ previously applied to the potassium chloride (or sodium chloride)–hydrochloric acid solutions, yet some adjustment of the constants is required. The solution volume of either the acid or the water is different, and if the value of K is retained at 1·01275, the expression

$$d_{4°}^{25°} = 1{\cdot}01275 + 0{\cdot}01355a + 0{\cdot}0193b \quad . \quad . \quad . \quad \text{(i)}$$

gives fair agreement for the calculated densities (see below). The corresponding solution volumes of the acid and the salt are 22·62 and 22·80, and the lithium ions show only a small apparent volume in solution. The apparent density of the water in the solutions is then the same as in those containing sodium chloride or potassiun chloride. This result, in the light of Masson's work (J., 1911, **99**, 1132), can only be regarded as conclusive if no other constants satisfy the expression. Examination of the data shows that the solution volumes of the lithium chloride and the acid are nearly equal. Assuming equality, and taking the value HCl = 22·43 as found in Part I, the values of the constants for the density expression may be deduced from this value together with that obtained for the water

from the equation $w\gamma + a\alpha + b\beta = 1000$, where α, β, and γ are the molar solution volumes of acid, salt, and water, and a, b, and w the molar concentrations per 1000 c.c. (Masson, *loc. cit.*). The mean value of γ is 17·82 ($\alpha = \beta = 22{\cdot}43$), and hence $K = d_w = 1{\cdot}0110$; k_1 and k_2 are then calculated from $k_1 = (M_a - \alpha d_w)/1000$ and $k_2 = (M_b - \beta d_w)/1000$, M_a being the molecular weight of the acid, and M_b that of the salt, and it is found that $k_1 = 0{\cdot}0138$ and $k_2 = 0{\cdot}0197$. The equation

$$d_{4^\circ}^{25^\circ} = 1{\cdot}0110 + 0{\cdot}0138a + 0{\cdot}0197b \quad . \quad . \quad . \quad \text{(ii)}$$

gives at least as good agreement as is obtained with the other values for the constants, as is shown by the following comparison.

$d_{4^\circ}^{25^\circ}$ (obs.)	1·1176	1·1147	1·1116	1·1087	1·1050
(calc., i)	1·1171	1·1150	1·1116	1·1082	1·1049
(calc., ii)	*1·1175*	*1·1153*	*1·1118*	*1·1084*	*1·1050*
$d_{4^\circ}^{25^\circ}$ (obs.)	1·1019	1·0985	1·0957	1·0920	1·0893
(calc., i)	1·1016	1·0984	1·0957	1·0921	1·0894
(calc., ii)	1·1016	1·0984	1·0955	1·0919	1·0891

It seems that this type of calculation is in the nature of a compromise, involving an assumption of constant solution volumes for the series of solutions, which is probably not strictly justifiable. The variations in the solution volumes, as calculated from the different constants, are, however, not very great, and are unimportant for the subsequent discussion of viscosities. The solution volumes may now conveniently be reviewed in tabular form and compared with values calculated from ionic radii. Calculations have been made in two ways: (1) The expression $\frac{4}{3}\pi r^3 N$ is used to obtain the ionic volume for the g.-ion, r being the radius as given by Wasastjerna (*Soc. Sci. Fenn. Comm. Phys. Math.*, 1923, **38**, 1) and N the Avogadro number. (2) It is assumed that the ionic volumes bear the same relationship to the solution volumes as does the bivalent oxygen atom (or ion) O″ to the water molecule, taken as 18; the molar volumes are then obtained by summing the ionic volumes. Conversely, the experimental solution volumes of the salts and the acid may be divided into the respective ionic solution volumes, the hydrogen ion in the case of the acid having no appreciable volume.

Ionic volumes.

	Li˙.	Na˙.	K˙.	Cl′.	O″ (H_2O).
r, in A.U.	0·72	1·01	1·30	1·72	1·32
r^3, ,,	0·373	1·030	2·197	5·088	2·300
$\frac{4}{3}\pi r^3 N$, in c.c.	0·946	2·616	5·578	12·92	5·84
$r^3 \times 18/2{\cdot}300$	2·921	8·063	17·60	39·83	18·00
ϕ (found) (i)	0·18	—	—	22·62	—
(ii)	0·0	—	—	22·43	17·82
(iii)	—	1·58	12·25	22·43	17·795
(iv)	0·33	—	—	22·58	17·795

The solution volumes found (ϕ) are those obtained according to the values adopted for the constants in the density calculations; thus (i) and (ii) are based on the values used in equations (i) and (ii) respectively, (iii) is based on the values used in Part I, and (iv) on the values $K = 1{\cdot}01275$, $k_1 = 0{\cdot}0136$, $k_2 = 0{\cdot}0192$.

Molar volumes.

	HCl.	LiCl.	NaCl.	KCl.	H_2O.
ϕ (found) (ii)	22·43	22·43	—	—	17·82
(iii)	22·43	—	24·00	34·66	17·795
(iv)	22·58	22·91	—	—	17·795
$\frac{4}{3}\pi(r_1^3 + r_2^3)N$ ...	12·921	13·87	15·54	18·50	5·84 (O″)
ϕ for solids	—	20·54	26·96	37·44	—

The values for the solids are derived from density data due to Baxter (*Amer. Chem. J.*, 1904, **31**, 558). Green (*loc. cit.*) obtained values for the solution volume of lithium chloride ranging from 17·53 to 20·94 according to the concentrations, the values in concentrated solution being in close agreement with Baxter's figure for the solid. Since Green's calculations involve the use of the density of pure water, no change in this value being allowed for in the concentrated solutions, it need not necessarily be concluded that the actual solution volume is the same as the solid volume. On the other hand, it is difficult to see why the solution volume obtained by the author (22·43) is higher than that of the solid—in the case of sodium and potassium chlorides the solution volumes are less than the solid volumes. The table shows also that the volumes deduced from the lattice radii are considerably less than the apparent solution volumes.

Viscosities.—The empirical method of calculating the degree of hydration of ions, as used in Part I, has been applied to the results for lithium chloride and leads to values which are comparable with those obtained for potassium and sodium. As expected, lithium chloride is more highly hydrated and the generally accepted series relationship $Li^{\cdot} > Na^{\cdot} > K^{\cdot}$ is indicated. The fall in viscosity which occurs when hydrochloric acid replaces lithium chloride is accounted for by assuming that the lithium ions are hydrated, whilst the hydrogen and chlorine ions are not solvated to any marked extent. Changes of viscosity due to changes of chlorine-ion concentration are expressed by the equation $\eta_1 - \eta_2 = \frac{1}{2}(\eta_1 + \eta_2) \times 2{\cdot}5\phi$, where ϕ is the volume of ions added to or removed from 1 c.c. of solution, and is given by $\phi = (C_2 - C_1) \times 22{\cdot}43/1000$. The volume 22·43 is that of the chlorine ion in solution. If the hydrogen ions have no specific effect, as appears to be the case for solutions of pure acid, then on comparing a solution of hydrochloric acid with one of lithium chloride of equal chlorine-ion concentration, complete dissociation

being assumed, any difference in viscosity may be attributed to the solvated lithium ions. It is further assumed that their effect is proportional to their volume, as with the chlorine ions, and the volnme of hydrated lithium ions is calculated from the above equation. The ϕ value so obtained is divided by the concentration of lithium chloride in solution, and this gives the effective volume of 1 g.-ion of lithium ions, from which the volume of water accompanying the 1 g.-ion is deduced. From the following data, *viz.*, $C = 5{\cdot}407$, $\eta(\text{LiCl}) = 0{\cdot}01951$, $\eta(\text{HCl}) = 0{\cdot}01220$ (from Green's data), $\phi = 0{\cdot}1829$ c.c. (or 182·9 c.c. per litre), one obtains in this way 33·82 c.c. per g.-ion of lithium, corresponding to a hydration with practically the same amount of water, since the lithium ion has an almost negligible solution volume; thus x, the hydration number, is 1·88. This value is decidedly higher than that obtained for sodium ions ($x = 1{\cdot}44$) in the same way and at practically the same concentration.

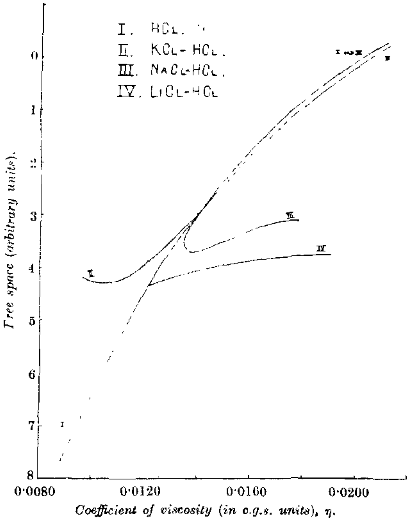
A more trustworthy result is probably obtained by calculating the hydration numbers for each successive pair of solutions in the series of salt and acid mixtures. The values so obtained are given in the last column of Table I. Any changes of chlorine-ion concentration are allowed for in making the calculations.

The above methods of calculatiug the degrees of hydration can only be regarded as trustworthy if it is shown that viscosity changes can be related to changes in the mean sizes of the molecules composing a liquid mixture. The original equation of Einstein $\eta = \eta_0(1 + 2{\cdot}5\phi)$ is not concerned with the actual size of the suspended particles, but deals with their total volume. Smoluchowski's extension of this equation (*Kolloid-Z.*, 1916, **18**, 194), introducing a correction for the charge upon the suspended particle, involves the radius; but in the present state of the knowledge of the applicability of this formula, it seems hardly possible to extend its use to the salt and acid solutions here considered. The problem may be approached from another point of view. Dunn (*Trans. Faraday Soc.*, 1926, **22**, 401) has developed a kinetic theory of viscosity of liquids, which, whilst it is primarily concerned with the effect of change of temperature, is of interest in that it deals with the attractive forces between the molecules and the factors governing the slipping between the planes. One of these factors is the possession by some of the molecules of a certain critical energy in virtue of which they are subject to negligible cohesion, and hence represent "loose spots" in the adjacent planes. It seems that the number of such molecules in a given liquid will depend partly upon the amount of free space. The question of the relation between free space and viscosity has been investigated by McLeod (*ibid.*, 1923,

19, 6), who suggested that for normal liquids viscosity should be inversely proportional to free space. It is of interest, therefore, to see how this bears upon the problem of the salt and acid solutions. It is essential to show that the variations of free space alone cannot account for the viscosity effects.

The molar volumes obtained by calculation from the lattice radii are taken as the limiting volumes of the various species, and for a

FIG. 1.



given solution the free space is calculated from the molar concentrations of salt, acid, and water (*i.e.*, 1000 — space occupied). Even if the resulting values are not numerically equal to the actual free space, they should be comparable amongst themselves. They are plotted against the viscosities in Fig. 1, the curve for hydrochloric acid being derived from Green's data (*loc. cit.*). The curves are very similar to those obtained by plotting total solute concentration against viscosity (see Fig. 3, Part I).

If the free space alone governed the viscosity, the changes would be in the direction of lower viscosity for greater free space. As acid displaces salt in the sodium chloride–acid solutions, the free space increases at first and the viscosity falls. The rate of fall is, however, much more rapid than for corresponding free-space change in pure acid solutions. At a later stage in the mixed solutions, free space decreases with increase of total solute concentration, and the curve finally becomes identical with that for pure acid.

The curve for the potassium chloride–acid mixtures shows that the free space at first increases whilst viscosity rises, and this is in accord with the idea that the latter effect is partly due to the substitution of larger water molecules for smaller potassium ions. The subsequent increase of viscosity may be more largely due to the decrease in free space.

Lithium chloride solutions have much higher viscosities than potassium chloride solutions of equal free space. The total solute concentrations are, however, also higher in this case.

When lithium chloride is compared with sodium chloride, it is seen that whilst the viscosities are comparable for solutions of approximately the same total concentration and the same relative amounts of salt and acid, yet those containing lithium chloride have more free space. The effect of the greater free space has been more than counterbalanced by the presence of the more highly hydrated lithium ions.

Summary and Conclusions.

1. Densities and viscosities have been determined at 25° for a series of concentrated mixed aqueous solutions of lithium chloride and hydrochloric acid. The methods of Scarpa and Ostwald for measuring viscosities have been again compared and found to agree.

2. Formulæ of the type $d = K' + k_1a + k_2b$ can be used to calculate the densities with fair accuracy. The assumption of the strict constancy of the molar solution volumes is not, however, justifiable. The packing of the ions amongst the water molecules may be supposed to involve a reduction of the free space depending upon the numbers and sizes of the various ions. The apparent volume of the water in solution may therefore vary from one solution to another.

3. The replacement of lithium chloride by hydrochloric acid results in a fall in viscosity which is interpreted as being due to the higher hydration of the lithium ions than of the hydrogen ions. Hydration numbers are calculated which indicate (i) a greater degree of hydration for lithium than sodium under similar conditions, (ii) a fall in the degree of hydration as the proportion of acid in the solution increases.

4. The influence of "free space" upon the viscosities in mixed solutions of lithium, sodium, or potassium chloride and hydrochloric acid is discussed.

The author wishes to record his thanks to Professor A. A. Boon for his kind interest and encouragement during these researches.

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CCCXVI.—*The Reduction of Selenious Acid.*

By LESLIE MARSHALL CLARK.

IT has long been known that when selenious acid is reduced in the presence of copper or other heavy metals, the precipitate obtained does not consist of selenium alone but contains in addition some metallic compound of selenium (compare Keller, *J. Amer. Chem. Soc.*, 1897, **19**, 773). This point has been particularly exemplified by examination of the solutions obtained after estimation of nitrogen by the Kjeldahl method in certain organic selenium compounds, copper having been added in the sulphuric acid–potassium sulphate treatment as usual to aid the destruction of the organic material. It was found if the alkaline solutions remaining after the distillation of ammonia were made very slightly acid with hydrochloric acid and reduced with sulphurous acid, a black precipitate was obtained which had the composition of cuprous selenide. Moreover, it is of interest that in all cases a very considerable loss of selenium had occurred during the destruction of the organic matter.

The reaction has now been further examined by reducing selenious acid by sulphurous acid in solutions containing copper sulphate and hydrochloric acid. The precipitate obtained varies from pure selenium, in solutions containing much hydrochloric acid, to cuprous selenide in dilute acid solutions, a mixture of the element and salt being formed intermediately (see table, p. 2391). The hydrochloric acid concentration is evidently the factor determining the composition of the precipitate (Expt. A). As a possible explanation of this phenomenon the following has to be considered. Selenious acid may be reduced by sulphurous acid with intermediate formation of hydrogen selenide, which reacts with a further amount of unchanged selenious acid to give selenium :

$$2H_2Se + SeO_2 = 2H_2O + 3Se \quad . \quad . \quad . \quad . \quad (1)$$

In the presence of cuprous ions, the hydrogen selenide will form cuprous selenide, but the amount of this compound formed will

depend on the hydrogen-ion concentration of the solution. This is largely determined by the hydrochloric acid concentration, which will also affect the rate of the reaction (1), increase of acid favouring the separation of selenium. The suggested intermediate reaction has been found to take place, for when hydrogen selenide is passed into an aqueous solution containing selenious acid, selenium is precipitated in the amount required by equation (1) (Expt. D). The mechanism which has been suggested above for the reduction of selenious acid may therefore be the correct one, but the experiment on the reaction between selenious acid and hydrogen selenide is not crucial, for the following reason. When finely ground metallic selenium is kept in contact with a hot solution of sulphurous acid containing copper sulphate, the selenium increases in weight owing to the formation of cuprous selenide (Expt. B). It has not been found possible to achieve complete conversion of the element into cuprous selenide, presumably owing to the arrest of further chemical action by the formation of a coating of selenide on the individual grains of selenium.

There is thus a secondary reaction between selenium, sulphurous acid, and copper sulphate in which cuprous selenide can be formed, and this makes it unnecessary to postulate the intermediate formation of hydrogen selenide when selenious acid is reduced. The fact that complete conversion of selenium into cuprous selenide cannot be brought about in Expt. B, whereas the theoretical amount of cuprous selenide can be obtained in the reduction of selenious acid when the proper hydrochloric acid concentration is present (see table), cannot be used as an argument against the hypothesis of this secondary reaction, for the red modification formed by the reduction of selenious acid possesses a higher degree of chemical reactivity than the metallic selenium powder used in Expt. B and is, moreover, in a much more finely divided condition.

Reinsch (Fresenius, " Qualitative Chemical Analysis," 10th Edtn., p. 118) observes that " metallic copper when placed in a warm solution of selenious acid containing hydrochloric acid becomes immediately coated black; if the solution remains long in contact with the copper it turns light red from the separation of selenium." These results are explicable on the theory that selenious acid is reduced to selenium by the cuprous ions formed at the copper–hydrochloric acid interface, and that this selenium is further reduced by cuprous ions to give cuprous selenide, the dark coating referred to by Reinsch. These reactions may be represented by the equations

$$SeO_2 + 2Cu_2Cl_2 + 4HCl = Se + 4CuCl_2 + 2H_2O \quad . \quad (2)$$

$$Se + 2Cu_2Cl_2 = Cu_2Se + 2CuCl_2 \quad . \quad . \quad . \quad . \quad (3)$$

The experiments on the formation of cuprous selenide already described suggested that the nature of the deposit produced on the copper would depend on the hydrochloric acid concentration. This was found to be the case (Expt. C), since when strips of copper are immersed in selenious acid solutions containing varying amounts of hydrochloric acid, the precipitate formed varies from pure selenium in high concentrations of acid to a black deposit of cuprous *selenide adhering to the copper in low concentrations.* The selenium formed in the most concentrated hydrochloric acid solution examined was slowly reduced to cuprous selenide, evidently by the cuprous chloride present.

The facts described in this communication may therefore be explained as follows: when selenions acid is reduced by sulphurous acid, reduction to the element probably occurs without intermediate formation of hydrogen selenide. The selenium so formed can be further reduced to cuprous selenide should cuprous ions be present in the solution, but the extent to which this can take place is determined by the hydrochloric acid concentration. It is probable that the hydrochloric acid affects the cuprous chloride concentration by formation of the known cuprous chloride–hydrochloric acid complex.

Evidently there is a close parallelism between these experiments and those described by Wardlaw and Pinkard (J., 1922, **121**, 216), who found that, in the reaction between sulphur dioxide and cuprous chloride dissolved in hydrochloric acid, there is some definite concentration of acid above which cuprous chloride and sulphur dioxide react with the separation of sulphnr only, an intermediate concentration of acid in which both sulphur and cuprous sulphide are precipitated, and a stage in which snlphide only is produced. These authors also showed that if the concentration of hydrochloric acid fell below 35 c.c. of concentrated acid to 215 c.c. of water, no reduction of sulphur dioxide by cuprous chloride took place. In the present case, however, reduction of selenious acid was found even when less than 1 c.c. of concentrated acid was present in 75 c.c. of water [Expt. C (1)].

It had been intended to obtain further tests of the theory now put forward (*e.g.*, by studying the reduction of selenious acid by various concentrations of cuprous chloride), but the work has had to be abandoned.

EXPERIMENTAL.

Expt. A.—To a solution of sodium selenite (5·000 g.) in boiled, distilled water, 10 c.c. of concentrated hydrochloric acid were added, and the volume was made up to 500 c.c.; 25 c.c. of this solution gave 0·1053 g. of selenium when reduced with sulphurous

acid in the presence of hydrochloric acid according to the usual method. Copper sulphate (1·25 g.) in water (75 c.c.) was added to each of a number of 25 c.c. portions of the selenite solution together with various amounts of hydrochloric acid: 30 c.c. of freshly prepared, *saturated aqueous solution of sulphur dioxide were then slowly poured into the hot mixture, which was kept gently boiling* for ½ *hour. Almost immediate precipitation occurred in each case*, the colour of the precipitate with the higher concentrations of hydrochloric acid being reddish brown, changing to black. A further 30 c.c. of sulphurous acid solution was added, and the mixture kept on the steam-bath for ½ hour longer. The precipitate was filtered on an asbestos mat in a Gooch crucible, well washed with sulphurous acid and water, dried in the steam oven, and weighed. (Moist cuprous selenide is quite stable to such a drying process, since when 0·2778 g. of the pure compound was moistened with water and dried as described, the residue was unchanged in weight.) The results are shown in the following table :

25 C.c. of the solution contain 0·1053 g. Se, equivalent to 0·2740 g. Cu_2Se.

HCl added, c.c.	Wt. of ppt., g.	Cu_2Se in ppt., %.	HCl added, c.c.	Wt. of ppt., g.	Cu_2Se in ppt., %.
1	0·2712	99	5	0.1680	61
2	0·2240	86	10	0·1266	27
3	0·2099	81	20	0·1076	3·5
4	0·1827	69	30	0·1050	0

Expt. B.—Reaction between selenium, copper sulphate, and sulphurous acid. Finely powdered selenium (0·1500 g.) was gently boiled for ½ hour with copper sulphate (2·0 g.) in water (100 c.c.) to which hydrochloric acid (1 c.c.) and saturated sulphurous acid (30 c.c.) had been added, 3 c.c. of ethyl alcohol having been added before addition of the sulphurous acid, so that the solution could wet the selenium powder, which otherwise made a film on the surface. Another 30 c.c. of sulphurous acid were added, and the mixture was kept on the steam-bath for 1 hour. The residue after filtration and drying weighed 0·3054 g. (Calc. for complete conversion into Cu_2Se, 0·3900 g.). A qualitative test showed that the precipitate contained selenium and copper, but no sulphur.

No change in the weight of another sample of selenium was observed when the above experiment was repeated without addition of sulphurous acid.

Expt. C.—Reduction of selenious acid by cuprous chloride. 25 C.c. *portions of a solution of 5·00 g. of sodium selenite in 250 c.c. of water containing 10 c.c. of hydrochloric acid were diluted with 50 c.c. of water, and varying amounts of* hydrochloric acid were added. *A piece of thin copper sheet (about 4 cm. square) was then introduced*

into each solution; reaction began almost immediately, but the delay was longest in the solution containing least hydrochloric acid:

(1) No extra hydrochloric acid added. The copper was rapidly completely coated with a black film.

(2) 1 C.c. of acid added. A black film was formed which flaked away after standing for some hours. After 24 hours some selenium was also being deposited.

(3) 5 C.c. of acid added. A reddish-brown deposit was formed, which clearly contained some red selenium, as well as cuprous selenide.

(4) 20 C.c. of acid added. Selenium was precipitated in a red cloud at the copper surface, but did not adhere thereto. After 24 hours the precipitate had darkened in colour, and then contained copper, but the filtered solution contained no selenium, complete reduction having been effected.

The formation of a mixture of red selenium and cuprous selenide described in Expts. C (2) and (3) would not be expected were the solution homogeneous. If the hydrochloric acid–cuprous chloride concentrations were such that selenium was partially reduced to cuprous selenide, then each particle of selenium would have a coating of the selenide and no red selenium would be distinguished. In the experiments in question, the results are ascribed to the presence of layers of solution which are not homogeneous in the vicinity of the copper plate. The hydrochloric acid and cuprous chloride contents of such layers will naturally vary with the distance of the layer from the metal and with time. The product of the reduction may then be non-homogeneous as described.

Expt. D.—Reaction between selenium dioxide and hydrogen selenide. A carefully dried, round-bottomed flask containing aluminium selenide was fitted with a funnel incorporating a three-way tap in order that water or hydrogen might be admitted at will. A tube from this flask dipped below a solution of selenium dioxide in cold, dilute, oxygen-free hydrochloric acid contained in a conical flask, from which a tube passed to a trap containing cadmium acetate solution for removal of uncombined hydrogen selenide. Dry hydrogen was passed through the apparatus for an hour to remove air, the gas was cut off, and cold, boiled, distilled water was admitted to the aluminium alloy. When sufficient water had been added, a slow stream of hydrogen was started to sweep the evolved gas through the reaction flask and thence into the cadmium acetate trap. Immediate reaction took place and selenium was deposited in the reaction flask. A rather colloidal precipitate of red selenium formed at first, but this slowly coagulated, leaving a clear aqueous

liquid in which flocculent masses of the element were suspended. After $1\frac{3}{4}$ hours, the selenium formed was rapidly filtered through a Gooch crucible, washed with water, dried, and weighed.

The reaction flask initially contained 60 c.c. of water, 10 c.c. of concentrated hydrochloric acid, and selenium dioxide corresponding to 0·0696 g. of selenium, and at the conclusion of the experiment 0·2168 g. of selenium was obtained from it. According to equation (1), selenious oxide corresponding to 0·0696 g. of selenium should react with hydrogen selenide to produce 0·2088 g. of the element. The error in other similar experiments was never greater than 4% and the agreement between the calculated and observed figures is sufficiently close to be accepted as confirmation of the equation.

I wish to thank Mr. G. C. H. Jenkins for assistance in some of the experiments described in this communication.

NORTHWICH RD., WEAVERHAM. [*Received, February 22nd, 1928.*]

CCCXVII.—*The Formation of 2-Substituted Benziminazoles.*

By MONTAGUE ALEXANDRA PHILLIPS.

IT has been shown (Phillips, this vol., p. 172) that 2-methylbenziminazoles are readily formed by the action of boiling dilute hydrochloric acid on mono- or di-acetyl-*o*-diamines and by the action of acetic anhydride and hydrochloric acid on *o*-phenylenediamines, and it was suggested that hydrolysis of the diacetyl to the monoacetyl compound constituted a stage in the formation of the ring compound from the former.

These reactions have now been extended to the formation of other 2-substituted benziminazoles, and it has been shown that *o*-phenylenediamine on condensation with formic, acetic, propionic, glycollic, lactic, and mandelic acids in the presence of boiling dilute hydrochloric acid gives good yields of the corresponding cyclic compound.

In view of the general nature of this reaction, it now seems possible, as an alternative to the above suggestion, that the mechanism of the formation of 2-substituted benziminazoles from mono- and di-acyl-*o*-diamines involves hydrolysis to the diamine with subsequent formation of the ring. Since traces of 4-nitro-*o*-phenylenediamine always seem to accompany 5-nitro-2-methylbenziminazole in the formation of the latter compound from 4-nitrodiacetyl-*o*-phenylenediamine (compare Phillips, *loc. cit.*) and the amount of diamine seems to be greater if the heating is not pro-

longed, it would seem that, in this case at least, the second view i the more correct. Experiments are contemplated which may decid between these two views.

The reduction of *o*-nitroacetanilide by iron and dilute acetic aci (a method which is generally employed for the production o *o*-aminoacylanilides) gives benziminazole only. The effect of a *p*-cyanomethyl group in stabilising the *o*-aminoformamido-structur is shown by the reduction of 3-nitro-4-formamidobenzyl cyanid by this method (Maron, Kontorowitsch, and Bloch, *Ber.*, 1914, **47** 1377; D.R.-P. 283,448).

3-Amino-4-formamidobenzyl cyanide, 3-amino-4-acetamidobenzy cyanide, and 3-amino-4-lactamidophenetole, which were shown b Maron and his co-workers (*loc. cit.*; *Ber.*, 1914, **47**, 718) to pas into the corresponding benziminazoles by prolonged treatment wit formic or glacial acetic acid, readily give the same ring compound by boiling with dilute hydrochloric acid. 3 : 4-Diformamidobenzy cyanide also gives the benziminazole readily by similar treatment.

The condensation of *o*-phenylenediamine and oxalic, malonic and succinic acids requires special notice. *o*-Phenylenediamine an oxalic acid in the presence of boiling dilute hydrochloric acid giv a quantitative yield of 2 : 3-*dihydroxyquinoxaline*, no benziminazol derivative being detected, whilst malonic acid and *o*-phenylene diamine give a mixture of *o*-phenylenemalonamide (I) (compare Meyer and co-workers, *Annalen*, 1906, **347**, 17) and 2-*aminomalon anilic acid* (II), which readily passes into the heterocyclic compoun on further treatment with boiling dilute mineral acid. No benz iminazole-2-acetic acid was detected.

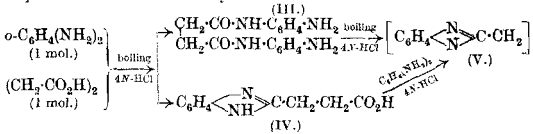
$$C_6H_4(NH_2)_2 + CH_2(CO_2H)_2 \longrightarrow$$

$$\text{(I.)}\ C_6H_4{<}^{NH\cdot CO}_{NH\cdot CO}{>}CH_2 + C_6H_4(NH_2)\cdot NH\cdot CO\cdot CH_2\cdot CO_2H\ \text{(II.)}$$

2 : 3-Dihydroxyquinoxaline and o-phenylenemalonamide resembl each other in their insolubility in water and organic solvents, i their high melting points, and in the formation of very sparingl soluble monosodium salts.

From succinic acid and *o*-phenylenediamine (1 mol. of each 2 : 2′-diaminosuccinanilide (III) and benziminazole-2-propionic aci (IV) were isolated, whilst with double the proportion of the diamine αβ-dibenziminazolylethane (V) and traces of benziminazole-2 propionic acid were found. αβ-Dibenziminazolylethane, originall obtained by Walther and von Pulawski (*J. pr. Chem.*, 1899, **59** 249) by the action of succinic anhydride on *o*-phenylenediamine a high temperatures, was also obtained from 2 : 2′-diaminosuccinanilid by treatment with hot dilute hydrochloric acid and by condensatio

of benziminazole-2-propionic acid and *o*-phenylenediamine in the presence of the same catalyst:



The synthesis of 2-phenylbenziminazole by the above methods has not proved practicable, only traces of this compound having been isolated as picrate by treatment of *o*-aminobenzanilide and dibenzoyl-*o*-phenylenediamine with boiling dilute hydrochloric acid. The condensation of *o*-phenylenediamine with benzoic acid, benzoic anhydride, or benzoyl chloride in the presence of the above catalyst was also unsuccessful (compare, however, Walther and von Pulawski, *loc. cit.*).

That these reactions are not confined to the aromatic diamines is suggested by the ready conversion of $\alpha\alpha'$-diacetylethylenediamine into 2-methyl-4 : 5-dihydroglyoxaline by boiling with dilute hydrochloric acid; it is proposed to study the formation of glyoxalines from diacylethylenediamines by the above methods.

EXPERIMENTAL.

Condensation of o-Phenylenediamine and Organic Acids in Presence of Boiling 4N-Hydrochloric Acid.

o-Phenylenediamine (0·02 mol.), the requisite acid (0·03 mol.), and 20 c.c. of 4*N*-hydrochloric acid were boiled for 30—40 minutes under reflux. On neutralisation of the filtered solution with ammonia, the benziminazole separated. In no case except that of lactic acid was the benziminazole isolated readily when the condensation was attempted in the absence of the mineral acid.

All the benziminazoles described in the following table are readily soluble in dilute mineral acids and in excess of dilute caustic alkalis. They were recrystallised from water except where otherwise indicated.

Acid.	Benziminazole.	Crystalline form.	M. p.	Yield, %.	N, %. Found.	N, %. Calc.
Formic.	Unsubstituted.	Plates.	170°	60	23·6	23·7
Acetic.	2-Methyl.	Prisms.	176	60	21·3	21·2
Propionic.	2-Ethyl.	Prisms.*	177	70	19·0	19·1
Glycollic.	2-Hydroxymethyl	Plates.*	171—172†	65	18·7	18·9
Lactic.	2-α-Hydroxyethyl.	Plates.	178—179†	70	17·3	17·3
Mandelic.	2-α-Hydroxybenzyl.	Diamond plates.*	202—203†	50	12·4	12·5
Benzoic.	2-Phenyl.	(Traces isolated as picrate, m. p. 280°.)				

* Recrystallised from 50% alcohol.
† Compare Bistrzycki and Przeworski, *Ber.*, 1912, **45**, 3483.

Benziminazole was also obtained by reduction of *o*-nitroformanilide, using the method described for the preparation of *o*-aminoacetanilide (Phillips, *loc. cit.*) (Found : N, 23·5%), and by the action of boiling 4*N*-hydrochloric acid on *o-phenylenediamine monoformate* (Found : N, 23·6%).

3-*Nitro*-4-*lactamidophenetole* was obtained by warming a mixture of 5 g. of 4-*l*-lactamidophenetole (lactophenin) and 10 c.c. of 16% nitric acid for 5 minutes at 40°; the gum formed was poured into water (100 c.c.) and the resulting solid crystallised from 50% alcohol (4·5 g., yellow needles, m. p. 115°). The nitro-compound was reduced by iron and boiling dilute acetic acid as described previously; the amino-compound (yield 60%) crystallised from water in needles, m. p. 135—136° (compare Maron and Bloch, *Ber.*, 1914, **47**, 718). 5-Ethoxy-2-(α-hydroxyethyl)benziminazole was obtained in 50% yield by treating the above amino-compound (2 g.) with boiling 4*N*-hydrochloric acid (10 c.c.) for 30 minutes, with subsequent neutralisation. It forms white plates, m. p. 170—171°, from water, and is readily soluble in dilute mineral acids and in excess of dilute caustic alkali (Found: N, 13·5. Calc. for $C_{11}H_{14}O_2N_2$: N, 13·6%).

3-Nitro-4-formamidobenzyl cyanide was made by cautiously adding 4-formamidobenzyl cyauide to ten times its weight of nitric acid (*d* 1·5) at 5—6°. The nitration mixture on being poured on crushed ice deposited the nitro-compound, which was collected and washed within ten minutes to avoid hydrolysis of the formyl group; it crystallised from 60% alcohol in yellow prisms, m. p. 151—152° (yield 86%). On reduction with iron and acetic acid (Phillips, *loc. cit.*), a 50% yield of 3-amino-4-formamidobenzyl cyanide was obtained; white needles, m. p. 124°, from water (Found : N, 23·8. Calc. for $C_9H_9ON_3$: N, 24·0%).

3 : 4-*Diformamidobenzyl Cyanide*.—3-Amiuo-4-formamidobenzyl cyanide (1·5 g.) and formic acid (98%, 2 c.c.) were heated under reflux for 20 minutes. After removal of excess formic acid, the gum was dissolved in alcohol, and the filtered solution allowed to evaporate in a vacuum. The semi-solid mass left was crystallised from alcohol–ether, 3 : 4-*diformamidobenzyl cyanide* being obtained as a hygroscopic, micro-crystalline solid, m. p. 92—95°, readily soluble in water, ethyl and methyl alcohols, and acetic and formic acids, but insoluble in ether or benzene (Found : N, 20·5. $C_{10}H_9O_2N_3$ requires N, 20·7%).

Nitration of 4-*Acetamidobenzyl Cyanide*.—This nitration was studied by Gabriel (*Ber.*, 1882, **15**, 836), who isolated only the 3-nitro-derivative; the following method led to the production of 4-acetamidophenylacetamide in addition. 4-Acetamidobenzyl cyan-

ide (8 g.) was fed slowly into nitric acid (*d* 1·5, 50 c.c.) at 5—10°, and then poured on ice; the gummy solid obtained was collected, dried at 50° (7 g.), and crystallised from 300 c.c. of 50% alcohol, 3 g. of crude 4-acetamidophenylacetamide, m. p. 212—215°, being obtained; further crystallisation gave the pure amide, m. p. 231° (compare Purgotti, *Gazzetta*, 1890, **20**, 599) (Found: N, 14·8. Calc.: N, 14·6%). The mother-liquors on concentration to half bulk gave deep golden-yellow plates of the nitro-compound, m. p. 112—113° (2 g.) (Found: N, 19·3. Calc.: N, 19·2%), slowly soluble in excess of dilute caustic alkalis to give an orange solution. 3-Amino-4-acetamidobenzyl cyanide was obtained by reduction of the above nitro-compound by iron and boiling dilute acetic acid. It forms white needles from hot water, m. p. 140° (compare Maron, Kontorowitz, and Bloch, *loc. cit.*) (Found: N, 22·4. Calc.: N, 22·2%).

5-Cyanomethylbenziminazole.—3-Amino-4-formamidobenzyl cyanide (1·5 g.) or 3 : 4-diformamidobenzyl cyanide (1·5 g.) was boiled under reflux with 4*N*-hydrochloric acid (10 c.c.) for 20 minutes. The crystals which separated on neutralisation and cooling were collected, washed, and crystallised from hot water. The yield was approximately 1·0 g. in either case (80%); 5-cyanomethylbenziminazole crystallises from hot water as anhydrous, diamond-shaped plates, m. p. 158—159° (compare Maron, Kontorowitz, and Bloch, *loc. cit.*) (Found: N, 26·8. Calc.: N, 26·7%).

5-Cyanomethyl-2-methylbenziminazole.—3-Amino-4-acetamidobenzyl cyanide (3 g.) was refluxed for 20—30 minutes with 20 c.c. of 4*N*-hydrochloric acid; on neutralisation and cooling, 5-cyanomethyl-2-methylbenziminazole separated (yield 65%); it crystallises from hot water in prisms, m. p. 206° (compare Maron, Kontorowitz, and Bloch, *loc. cit.*).

Condensation of o-*Phenylenediamine and Dibasic Organic Acids in Presence of Boiling* 4N-*Hydrochloric Acid.*

Oxalic acid. *o*-Phenylenediamine (5·5 g.), oxalic acid (dihydrate, 6·5 g.), and 4*N*-hydrochloric acid (30 c.c.) were heated to boiling, and a crystalline solid formed. After 10 minutes' further boiling, the reaction mixture was cooled and the solid, consisting of almost pure 2 : 3-dihydroxyquinoxaline, was collected, washed with water, and dried (yield, 8 g.) (Found: N, 17·4%). The *sodium* salt was obtained as white prisms, sparingly soluble in hot water (Found: N, 15·5; Na, 12·15. $C_8H_5O_2N_2Na$ requires N, 15·2; Na, 12·5%), and, on acidification with hydrochloric acid, it gave the pure *quinoxaline* as white needles, insoluble in hot water or the ordinary solvents and not melting below 350° (Found: N, 17·4.

$C_8H_6O_2N_2$ requires N, 17·3%). That this compound is not the isomeric benziminazole-2-carboxylic acid is indicated by its weak acidity and by the sparing solubility of its sodium salt. Moreover, *benziminazole-2-carboxylic acid has been obtained by oxidation* of 2-methylbenziminazole (Bistrzycki and Przeworski, *loc. cit.*). The analogous 2 : 3-dihydroxyquinoxaline-6-arsinic acid, made from 3 : 4-diaminophenylarsinic acid by the above method, gives an arsono-compound which is insoluble in caustic alkali or alkali carbonate solutions, showing that this cannot be a benziminazole derivative (unpublished work).

Malonic acid. *o*-Phenylenediamine (5 g.), malonic acid (5 g.), and 4*N*-hydrochloric acid (30 c.c.) were boiled under reflux for 30 minutes. A white crystalline precipitate which had separated from the hot solution was collected after cooling (A); the filtrate on being made alkaline to litmus with 50% sodium hydroxide solution gave a crystalline precipitate (B). The solid A was further purified by means of its *mono-sodium* salt (compare dihydroxyquinoxaline, above), white, sparingly soluble cubes (Found : N, 14·5; Na, 11·4. $C_9H_7O_2N_2Na$ requires N, 14·1; Na, 11·6%), and was proved to be *o*-phenylenemalonamide (Found : N, 15·9. Calc. : N, 15·9%), white prisms, m. p. over 300°, insoluble in boiling water and the ordinary solvents, resembling dihydroxyquinoxaline in these particulars. The solid B (1·5 g.) crystallised from boiling water as white prisms of 2-*aminomalonanilic acid*, m. p. 175—176° (Found : N, 14·4. $C_9H_{10}O_3N_2$ requires N, 14·4%), an amphoteric substance; when its solution in dilute hydrochloric acid is boiled for ½ hour, *o*-phenylenemalonamide is formed in quantitative yield.

Succinic acid. (i) *o*-Phenylenediamine (8 g.), succinic acid (10 g.), and 4*N*-hydrochloric acid (60 c.c.) were boiled under reflux for 40 minutes. On cooling, a crystalline solid (A) separated. The filtrate on basification with 50% sodium hydroxide gave an amorphous precipitate (B); the filtrate from this, on neutralisation to Congo-red with hydrochloric acid, gave a crystalline precipitate (C). The last precipitate (4·5 g.) was further crystallised from hot water and shown to be benziminazole-2-propionic acid, white prisms, m. p. 224°, sparingly soluble in cold but readily soluble in boiling water, in dilute mineral acids, and in ammonia, sodium carbonate, etc. The solid A (9 g.) consisted of a mixture of succinic acid with the hydrochloride of the base B. The latter (2 g.) was found to be 2 : 2′-diaminosuccinanilide (compare Meyer, *Annalen*, 1903, **327**, 1), a white, amorphous solid, m. p. above 300°, insoluble in boiling water and in the ordinary solvents; its hydrochloride is sparingly soluble in cold water, from which it forms white, hexagonal plates (Found : N, 15·3; Cl, 19·1. Calc. : N, 15·1; Cl, 19·1%).

No trace of *o*-phenylenesuccinamide or of 2-aminosuccinanilic acid was detected.

(ii) *o*-Phenylenediamine (4·2 g., 2 mols.) and succinic acid (2·3 g., 1 mol.) were boiled for 1 hour with 4*N*-hydrochloric acid (30 c.c.). The solid which was precipitated on cooling was collected and crystallised from hot water (A); the filtrate on neutralisation to litmus gave 0·5 g. of benziminazole-2-propionic acid. The solid A (1·5 g.) was shown to be αβ-dibenziminazolylethane dihydrochloride (Found: N, 16·5; Cl, 20·9. Calc.: N, 16·7; Cl, 21·2%), white needles, sparingly soluble in water; this was also obtained by boiling for 1 hour under reflux a mixture of benziminazole-2-propionic acid (2 g.), *o*-phenylenediamine (1 g.), and 4*N*-hydrochloric acid (14 c.c.), and cooling (Found: N, 16·3; Cl, 20·9%), or by treatment of 2 : 2′-diaminosuccinanilide with boiling 4*N*-hydrochloric acid. The base is a white amorphous solid, m. p. above 300°.

2-*Methyl*-4 : 5-*dihydroglyoxaline*.—Diacetylethylenediamine, made by reduction of aminoacetonitrile hydrochloride (Fargher, J., 1920, **117**, 1351), followed by acetylation, was boiled for 30 minutes with five times its weight of 4*N*-hydrochloric acid and gave a 55% yield of the above glyoxaline, m. p. 107° (Found: N, 33·0. Calc.: N, 33·3%).

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WANDSWORTH, S.W. 18. [*Received, June 16th*, 1928.]

CCCXVIII.—*The Influence of Intensive Drying on Inner Equilibria. Part III.*

By ANDREAS SMITS.

THE author's theory of allotropy (*Chem. Weekblad*, 1910, **7**, 79, 155; *Versl. Akad. Wetensch. Amsterdam*, 1910, **18**, 808; *Z. physikal. Chem.*, 1911, **76**, 421) is based on a hypothesis consisting of two parts. The first part states that every phase, and therefore also every crystalline phase, of an allotropic substance is a state which in certain circumstances can behave as a poly-component phase. The second part states that this behaviour must be attributed to complexity, *i.e.*, to the existence of different molecular species; when these are in inner equilibrium, however, the behaviour of the system is unary, *i.e.*, it behaves as a one-component system.

When this theory was published, it was pointed out that such a single substance would be expected to behave as a poly-component phase under two conditions, *viz.*, during rapid working or by use of a negative catalyst.

In 1912 (J., **101**, 2339) H. B. Baker and Mrs. Baker showed that intensive drying had the effect of raising the boiling points of nitrogen trioxide and nitrogen tetroxide by 44° and 47° respectively. These results, which were unknown to me until 1921, seemed to indicate that *in the moist liquid an inner equilibrium exists between different species of molecules* (simple and complex molecules), and that either this inner equilibrium was fixed or the inner transformations were *retarded by intensive drying*.

In these experiments it seemed therefore that we had a very distinct confirmation of the theory of allotropy, and that intensive *drying was an excellent method of proving the complexity of a* so-called single substance (*Z. physikal. Chem.*, 1922, **100**, 477). The results published by Baker (J., 1922, **121**, 568), showing a great *elevation of boiling point in ten liquids that had been intensively* dried for several years, supplied a further confirmation of the theory, since several of these liquids were regarded as quite normal, single *substances. This increase in boiling point might possibly have been* ascribed to great superheating (rendered possible in some unknown way by intensive drying, see p. 2407), had not Baker found exactly *parallel effects in the surface tension and vapour density, the latter* being 2—3 times that found with moist liquids (this vol., p. 1051).

These results seemed to point to an inner equilibrium between different species of molecules in the moist liquid, as postulated by the theory. To explain the behaviour of the intensively dried substances as a whole, the author assumed that intensive drying causes first a retardation of the velocity of the establishment of, and possibly also a displacement of, the inner equilibrium, and finally a fixation of it ("The Theory of Allotropy," 1922, p. 310; J., 1924, **125**, 1068).

Although this hypothesis was very probable, it still lacked a direct proof. The author therefore studied the influence of intensive drying on the vapour pressure. If the establishment of inner equilibrium is retarded, it will be manifested by a retarded change of the vapour pressure with temperature and by a temporary decrease of the vapour pressure after partial distillation.

A displacement of the inner equilibrium, however, will be revealed by a change of the vapour pressure at constant temperature, whilst a fixation of the inuer equilibrium, as the final state of the process *of intensive drying*, should enable us to separate completely the different molecular species of the so-called single substance.

I wish to state emphatically that these studies can give us a proof *of the explanation of the intensive drying* which I *have advanced*. These considerations explain the behaviour of dried substances without making any special assumptions about the "mechanism"

of the action of the water molecules, as indeed every thermodynamical consideration does. A theory about that " mechanism " *will undoubtedly be advanced before very long; it will not displace* the present theory, however, but will complete it. It is necessary to emphasise this point because it seems that some confusion still exists on the matter.

(1) *Discussion of Vapour-density and Vapour-pressure Determinations.*

In an earlier paper we showed that intensively dried hexane in rapid evaporation behaved as a mixture, and we will shortly publish a detailed confirmation of this fact. Also, changes of vapour pressure at constant temperature, and without distillation, have been found in some cases, but even after several years' drying these changes are relatively small. On the other hand, Baker's experiments on the abnormally high vapour densities (*loc. cit.*) seem to contradict these results.

It was most unlikely that our carefully purified liquids, dried in *either small or large apparatus for 2—5 years with a relative very* large quantity of purest distilled phosphorus pentoxide, would be less completely dried than those of Baker; and it was therefore probable that there was some simple explanation of this apparent contradiction. Since studies of "velocity" phenomena, such as rapid distillation and rapid heating, showed rather large effects, whilst " equilibrium " phenomena, such as the vapour pressure, revealed little or no effect, it was obvious that the anomaly would disappear if the properties studied by Baker were actually velocity phenomena.

In reviewing Baker's experiments, we will discuss first his determination of the vapour density by the method of Victor Meyer, taking a simple example, such as nitrogen tetroxide; the P–x diagram of the pseudo-system at the temperature at which the experiment is carried out is given in Fig. 1 (see *op. cit.*, p. 24, Fig. 32).* Supposing now that, if in inner equilibrium at the given temperature, the coexisting phases are L and G, these phases will be present if the little bulb, used in Victor Meyer's method, is filled with moist nitrogen tetroxide. Further, we will suppose that the horizontal line p_1p_1 corresponds with a pressure of 1 atmosphere. If the bulb is broken, the liquid evaporates, but that evaporation is accompanied by a chemical transformation, namely, $N_2O_4 \rightarrow 2NO_2$, and the unsaturated vapour formed is given by the point G_1, lying on the vapour curve GG_0 of the unary figure, so that the composition

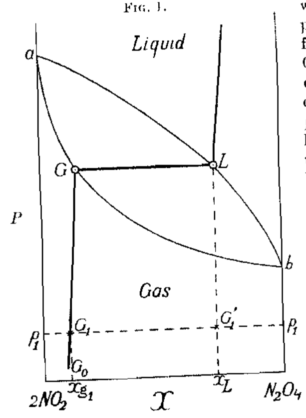
* The only difference is that the temperature corresponding with Fig. 32 is above the critical temperature of the pseudo-component a.

4 K

of the vapour formed is not x_L but x_{G_1}, and it is to this composition that the vapour density found corresponds.

If, however, the nitrogen tetroxide is so intensely dried that, although the inner equilibrium is not yet fixed, the inner transformations are distinctly retarded, the result of the vapour-density determination will now be quite different. This time, when the little bulb is broken, the liquid will to some extent behave as a mixture. Let us suppose, on the one hand, that the liquid behaves as a real mixture: in this case the reaction $N_2O_4 \longrightarrow 2NO_2$ will not take place, and if all the liquid is evaporated, a gas phase G_1' will be formed, the composition of which is equal to the composition of the liquid before the bulb was broken. Consequently, the vapour density found will then correspond with the composition x_L. On the other hand, it is now evident that, if the inner equilibrium is not yet fixed but the inner transformations are only retarded, the composition of the gas phase, at the moment of the reading, will be given by a point between G_1 and G_1'; consequently in this case the vapour density will show an abnormally high value, notwithstanding that the inner transformations are not yet stopped, but only retarded. If it had been possible to wait until the slow substance had reached inner equilibrium before the readings were taken, the ordinary vapour density would have been found, but in this method readings had to be taken quickly, so as to avoid errors due to the diffusion of the vapour into the air column.

FIG. 1.

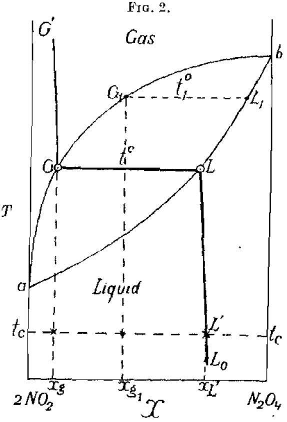


Hence, we see that vapour density, as determined by the Victor Meyer method, gives a value corresponding to a velocity phenomenon and that this method makes it possible to obtain large changes of the vapour density, since it enables us to find *temporary changes* which disappear if one waits until inner equilibrium in the gas phase is established. Similar results would be obtained by Dumas' method

The vapour pressure of the same dried liquid, at constant temperature, however, is an equilibrium phenomenon, and is still completely unchanged.

It is evident that the determination of the latent heat of vaporisation or condensation is the determination of the effect of a velocity phenomenon, and, indeed, it seems one of the best methods for finding *whether a retardation of the inner transformation has already occurred.* Considering a T–x diagram for constant pressure, say 1 atm. (Fig. 2; see also *op. cit.*, p. 27, upper part of Fig. 38), we see that in the pseudo-diagram the unary figure is given by the curves L_0L and GG' and the horizontal line GL; consequently L and G are the coexisting liquid and gas phases at the boiling point.

Fig. 2.



Suppose now that we determine the heat of condensation, and the temperature of the calorimeter corresponds with the horizontal line t_ct_c, we have to consider two cases. (1) If the substance behaves in a *unary* manner, the vapour phase G will be transformed into the liquid phase L', lying on the curve LL_0, and the heat of condensation therefore contains an exothermic heat of reaction corresponding with the change of composition from x_g to $x_{L'}$. (2) If, however, the substance has become slow, by intensive drying, and therefore behaves to some extent as a mixture, the point representing the boiling liquid will move along the curve Lb and that of the vapour phase along the curve Gb in such a way that the coexisting phases always lie on the same horizontal line—if the boiling point is increased, for instance, from $t°$ to $t_1°$, the coexisting phases are L_1 and G_1. Now it is evident that the condensation of the vapour phase G_1 in the calorimeter will give rise to a smaller heat of condensation, since the composition of this vapour phase x_{g_1} is nearer to $x_{L'}$ than is x_G, so that, although the composition of the condensed vapours lies between x_g and x_{g_1}, the exothermal chemical reaction is smaller than

in the first case, in which the substance was assumed to behave in a unary manner.

The following observations may be made on the enormous increase in the boiling points of intensively dried liquids observed by Baker. The apparatus contained two distilling flasks, each with two side tubes, and to one of these tubes was sealed the side piece of the other. In the determination of the boiling point, the liquid was distilled by heating the containing flask in an oil-bath, the other flask being cooled in water or in ice. When sufficient liquid had collected in the second flask, this was heated in the oil-bath while the first was cooled. That, after ten years' drying, the inner equilibrium was not yet fixed and the liquid behaved, on evaporation, as a mixture, follows from a remarkable fact mentioned by Baker himself (J., 1922, **121**, 568), namely, that when the condensed liquid from the distillation was again heated, it did not enter into a state of ebullition until the abnormally high temperature had been reached. Further, speaking of his result obtained with benzene, he says (*loc. cit.*), "The liquid boiled at 106° quite steadily. Some of the liquid was distilled from the apparatus into a distilling flask and left for a day exposed to moist air. Its boiling point was found to be 105°." The boiling point of the distillate was consequently the same as that of the residue and was still unchanged after a day in contact with moist air. If the inner equilibrium had been fixed, a distillate with abnormally low boiling point would have been formed, whereas both experiments indicate that just the opposite occurred, thus proving that the inner transformations had been merely retarded, so that the liquid on distillation behaves as a mixture. But since the transformations are not stopped, the inner equilibrium will after some time be re-established in the distillate, which will then show the same behaviour as the initial liquid. The second experiment proves that, notwithstanding the contact with moist air, the liquid was still slow.

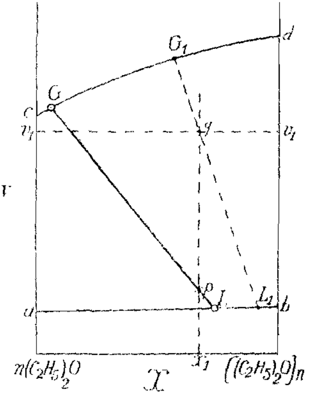
The following experiment indicates the same thing.

I wrote to Prof. Baker that I was very anxious to know what the vapour pressures of his dried liquids were, and he kindly determined that of dried ether, using a dried barometer tube of mercury, surrounded by a water jacket. On being admitted to the tube, the ether gave at 20° a vapour pressure of 374 mm. Hg instead of 442 mm., but this value rose slowly. This also is completely in agreement with a slow establishment of the inner equilibrium, which can be understood most easily by using a diagram (Fig. 3) in which the molecular volume V is plotted against the composition x (expressed, for instance, as mols.%). The temperature considered is that at which the vapour-pressure determination is carried out.

At this temperature, a is the volume of n g.-mols. of pure liquid

$(C_2H_5)_2O$, *i.e.*, liquid consisting only of the first pseudo-component [the single molecules $(C_2H_5)_2O$], or the completely dissociated second pseudo-component, under its own vapour pressure, and *c* is the volume of *n* g.-mols. of gaseous $(C_2H_5)_2O$ in equilibrium with this liquid phase. The points *b* and *d* have the same significance with respect to 1 g.-mol. of the second pseudo-component, $[(C_2H_5)_2O]_n$. The vapour pressure of pure liquid $(C_2H_5)_2O$ will be much larger than that of pure liquid $[(C_2H_5)_2O]_n$, and the molecular volume of the coexisting vapour is therefore much smaller than that of the vapour coexisting with $[(C_2H_5)_2O]_n$. In Fig. 3 it is supposed that the difference is so large (which is quite possible) that *n* times the molecular volume of the vapour coexisting with liquid $(C_2H_5)_2O$ is even smaller than the molecular volume of the vapour coexisting with liquid $[(C_2H_5)_2O]_n$, but this is not essential. The line *ab*, the binodal for the liquids, gives the molecular volumes of the liquid mixtures, whilst *cd*, the binodal for the vapours, gives the molecular volumes of the gaseous mixtures of the pseudo-system. *If the system of all these liquids and vapours behaves in a unary manner only one liquid and one vapour coexist*, namely those given by the points *L* and *G*. From the situation of these coexisting phases we see that the liquid phase is rich in the polymeric or complex molecules, whilst the vapour phase is rich in the single molecules. This coexistence corresponds to a definite pressure, the vapour pressure of the liquid in inner equilibrium.

FIG. 3.



Suppose now that the bulb with dried ether was nearly completely filled, *i.e.*, the volume of vapour was relatively very small. Drawing the nodal line *LG*, we can conclude from this that the state of the mixture must be represented by a point on this line and quite near to *L*, so that the total composition corresponds with x_1, for in this

case the quantities of the phases L and G, which together form the system are in the ratio Gp/Lp. After the bulb is broken, the system attains a relatively large volume, given, say, by the horizontal line v_1v_1; then we see that, if in the first moments the substance behaves as a *mixture*, owing to its sluggishness caused by intensive drying, the point q can tell us what the state of the coexisting phases will be during the first moments. For the state of a mixture of composition x_1 at a volume v_1 is given by the point q on the nodal line L_1G_1, and from the position of this point we see that the quantities of the coexisting phases are largely changed and the the ratio has now become G_1q/L_1q. This nodal line is situated in the region of lower pressures, so that the vapour pressure will be abnormally low. But as the inner equilibrium is not yet fixed, the inner transformations, which are only strongly retarded, are taking place in the direction of the inner equilibrium, which will be reached after some time, *i.e.*, the vapour pressure will increase.

In the experiments of Prof. and Mrs. Baker on nitrogen trioxide and nitrogen tetroxide a similar phenomenon took place. Directly after the bulb is broken the liquid must evaporate strongly, changing the composition of the coexisting phases in the direction of lower vapour pressure, *i.e.*, higher boiling points, and as the boiling liquid slowly distils, the behaviour as a mixture is continued.

(2) *Discussion of Surface-tension Determinations.*

We have now to deal with the determination of the surface tension; it is true that this is not a velocity phenomenon but this property is not trustworthy in this case for the following reasons. Baker (this vol., p. 1055) describes experiments in which a tube of 1 cm. diameter was prepared with two platinum plates 7 cm. long fixed facing each other at the lower end of the tube, and having a thermometer placed between them. Benzene was introduced just to cover the plates, which were connected with a 400-volt battery for some hours, and its boiling point was thus raised to 91°. This effect was not destroyed when the apparatus stood for a few days with the plates disconnected from the battery—the boiling point was 88° and the boiling was steady, not violent. While the boiling was proceeding, the voltage was again applied and within 2 minutes the evolution of bubbles was stopped. Measurements of the surface tension of the liquid indicated a 2—3-fold increase in molecular weight.

I had previously carried out sparking experiments and had been impressed by the efficiency of strong electric fields in drying dielectrics, but had delayed their application in this direction. I therefore repeated Baker's experiment (in collaboration with my

assistant Mr. Bruin), using an apparatus of exactly the same dimensions. Before the platinum plates were connected with the 400-volt battery, the boiling point of the benzene was 80·5°, and after the current had passed for 4 hours the boiling point had risen to 95° but then sank to 88° under steady boiling, even if the platinum plates were disconnected from the battery. The electrodes were now connected together, and after 2 days the boiling point was again determined, without applying an electrical field: it was still high (*viz.*, 93°), but sank again to 88° under steady boiling. The bubbles originated from a small part of the platinum wire, fixed to one of the plates.

Now it is known that the most favourable condition for superheating is to heat in a bath, and the best way to prevent superheating is to heat with a small flame applied at a point on the bulb containing the liquid. When heating was effected in the latter way, with application of the electrical field, the benzene boiled at 80·5° and the phenomenon mentioned by Baker had disappeared completely, thus showing that his high boiling points may be affected to an unknown degree by superheating.

At tbe same time we determined the influence of an electrical field on the vapour pressure, since if such a field had any influence on the position of the inner equilibrium, it would also change the vapour pressure. A similar tube with platinum plates was connected to a glass-spring indicator and to a little bulb containing phosphoric oxide. Benzene was introduced in the tube so as just to cover the plates. The apparatus was highly evacuated, and, without application of an electrical field, the vapour pressure was determined over the range 40—90°. The experiment was then repeated, applying an electrical field, first of 400 volts and then of 800 volts. The result was that the vapour-pressure lines coincided *completely*. From this we may conclnde that the electrical field does not effect any change in the inner equilibrium, and that the increase in boiling point is most probably due to the removal of electrically charged dust particles by the field, in which case superheating occurs more easily when heating is carried out in a bath. Hence we must infer that, had Baker heated the liquid with a very small flame (micro-burner), instead of in a bath, he would have found a normal boiling point for his dust-free liquid.

From his surface tension measurements, Baker calculated that the molecular weight was 2—3 times the normal, but the vapour-pressure determination, and, we may now add, also the boiling-point measurements, showed that the inner state of the liquid is not changed at all. Therefore it seems most probable that, if a liquid by long standing in a sealed tube has become free from dust particles,

the surface tension may be changed, and is therefore no longer a trustworthy criterion as to the state of the inner equilibrium.

Conclusions.

Consequently, my conclusions are : (1) That as yet neither Baker nor I have stopped the inner transformations in the *liquid* phase of a single substance but we have succeeded, as shown especially by Baker's determination of vapour density and latent heat, in retarding the velocity of the inner transformations by intensive drying of liquids, so that the substance behaves as a mixture with regard to what we have termed velocity phenomena. (2) Moreover, we have realised a fixation of the inner equilibrium in the *solid* phase and in the coexisting gas phase of a single substance by intensively drying sulphur trioxide, and our continued investigation of phosphoric oxide points to the same result. (3) With regard to the *gas* phase of a single substance, it is most probable that Baker, using small quantities, has realised a fixation.

In answer to the question whether intensive drying can effect a displacement of the inner equilibrium, we can say that in some cases relatively small displacements are found with liquids, that Baker most probably has realised a very strong displacement with gases, and that we have found a very distinct change in the case of ammonium chloride (preliminary paper, *Rec. trav. chim.*, 1927, **46**, 445).

Summary.

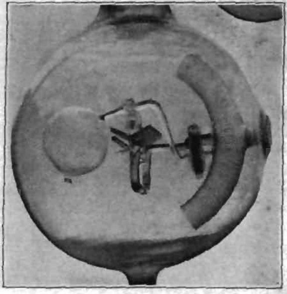
The present state of our knowledge of intensive drying is discussed. It is pointed out that intensively dried hexane in rapid distillation behaves as a mixture, but that the changes of vapour pressure at constant temperature, without distillation, are relatively small even after several years' drying. This appears to be in conflict with experiments in which Baker obtained abnormally high vapour densities for perfectly dry liquids. In seeking an explanation of this anomaly, it is seen that rapid evaporation and distillation are "velocity" phenomena, whereas vapour pressure is an "equilibrium" phenomenon, and that large effects are to be expected in the former case and negligible or zero effects in the latter. The two types of result are therefore reconciled.

Baker's surface-tension experiments alone appeared to present a difficulty, but it has now been shown that this property is *not* a trustworthy criterion for internal equilibrium, for it may be altered by removal of dust particles from a liquid during long standing.

Further, it has been demonstrated experimentally that an electric field has no influence on the vapour pressure of benzene or on its

FIG. 1.

FIG. 2.



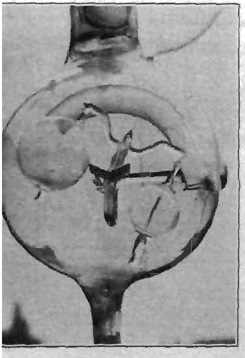


FIG. 3.

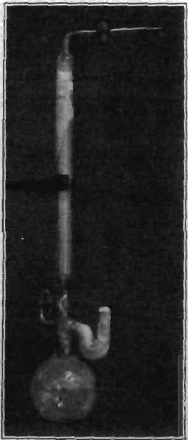


FIG. 4.

[To face p. 2409.]

boiling point, provided that, during the determination of the latter, superheating be avoided by the use of a small flame instead of a bath. Our recent results will be published shortly.

UNIVERSITY, AMSTERDAM. [*Received, June 25th*, 1928.]

CCCXIX.—*The Densi-Tensimeter.*

By ANDREAS SMITS.

EVER since Abegg (*Z. physikal. Chem.*, 1908, **61**, 455) emphasised the anomaly that ammonium chloride has the same sublimation pressure when perfectly dry as when moist, whilst the dried vapour was found undissociated and the moist almost completely dissociated, I have desired to repeat Johnson's experiments (*ibid.*, p. 457), but in a more trustworthy apparatus. The problem was to measure the vapour pressure and the vapour density simultaneously, but the insertion of a small baroscope into a vapour-pressure apparatus, with a glass-spring indicator, appeared to present insuperable difficulties, and it was not until the need for such an apparatus became imperative during our experiments on intensive drying, that one of my glass-blowers succeeded in the task. He introduced a quartz baroscope with a quartz knife-edge and also a graduated glass scale into a bulb of high-melting Jena glass of about 10 cm. diameter, so that this bulb formed part of a vapour-pressure apparatus having a glass-spring indicator, and a preliminary investigation was conducted on the "ammonium chloride" problem (*Rec. trav. chim.*, 1927, **46**, 445).

The apparatus has now been improved in certain directions. In the first place the pan on which the knife-edge rests was made from a tube which was cut in two lengthwise and turned up at the ends, to prevent the knife from slipping from the pan. This is seen in Fig. 1, which also shows a cross-piece in the right arm of the baroscope, the vertical tube of which is provided with a small steel rod embedded in powdered iron oxide; this steel rod serves to make the baroscope swing with the aid of a magnet, whereby it can be seen whether the deviation is reproducible.

The difficulty, however, was that in this form of the apparatus the pan could not be ground, whereas the knife-edge was. This was unfavourable, and I therefore changed the construction slightly (see Fig. 2).

Just above the knife-edge two thin quartz arms were sealed and bent down, so that these little arms prevented the baroscope from slipping from the pan, and consequently the pan could have an open V-form and thus be well ground, which was a great advantage. (The firm of Beckerson, Dieren, Holland, carried out the grinding of

the knife-edges and pans very efficiently.) The baroscope moved as regularly as a fine balance, and the calibration showed that the readings were exactly reproducible.

Another improvement was then made to ensure that, on cleaning, the baroscope is not removed from its place and made to float on the cleaning liquid. For this purpose the ends of the two little side arms, mentioned above, are bent horizontally, and a glass rod is sealed to the pan holder in such a way that, if the bulb of the baroscope is lifted by the cleaning liquid, the horizontal ends of the side arms are caught by this rod; the knife-edge now cannot be lifted up from the pan and the baroscope remains in the right position (see Fig. 2).

Although the apparatus was now very satisfactory, I thought that possibly the accuracy could be increased a little by changing the baroscope once more. In order to eliminate a possible source of slight error, caused by adsorption of vapour on the quartz surface of the baroscope, it was necessary to have, as accurately and symmetrically as possible, the same area of quartz surface on each side of the knife-edge. To ensure this, the baroscope of the latest construction contains two bulbs, but whilst the left one is closed, the right one has two or more holes, so that it can serve to enlarge the surface of the right part of the baroscope without impairing its function in the apparatus; moreover, since both the inner and the outer surface of the open bulb are exposed to the vapour, this bulb must be smaller than the other.

This principle is embodied in the baroscope shown in Fig. 3, from which we see also that the tube with the small iron rod is now sealed into the open bulb, that the needle is sealed at the middle of the arm of the baroscope, and that the scale is at the upper part of the apparatus.

Fig. 4 shows the bulb, containing the baroscope, sealed to the glass-spring indicator. The whole apparatus has been called a "Densi-Tensimeter."

THE UNIVERSITY, AMSTERDAM. [*Received, June 25th*, 1928.]

CCCXX.—*The Action of Substituted Aromatic Amines on Camphoric Anhydride. Bromo- and Iodo-camphoranilic Acids and Camphoro-bromo- and iodo-phenylimides.*

By MAHAN SINGH, RAM SINGH AHUJA, and KISHEN LAL.

WHEN a substituted aniline is condensed with camphoric anhydride, a camphoranilic acid and the corresponding imide are formed, the relative quantities depending on the nature of the substituent (R)

and its position in the amine (Singh and Singh, J., 1927, 1994; see also J., 1925, **127**, 1966). The order in which the *o*-, *m*-, and *p*-substituted amines affect the yield of the camphorimide is, however, not consistent for R = Cl, Br, I, Me, and CO_2H.

The results obtained from the condensation products of camphoric anhydride with bromoanilines and iodoanilines are now reported. Table I gives the approximate percentage yields of the respective camphorimides, formed together with carboxy-, methyl-, chloro-, bromo-, and iodo-camphoranilic acids.

TABLE I.

Percentage yields of the imides.

	CO_2H.	Me.	Cl.	I.	Br.
p	Nil	Traces	15—20	25—30	40
m	,,	—	6	31	25
o	,,	—	5	—	5—10

Except for the position of chlorine, the order for the *p*-substituted amines corresponds to the order which indicates the relative influence of the substituents on the nitration of a monosubstituted benzene. The ratio acid/imide produced is also dependent on the temperature at which the reaction is carried out, though the order in which the substituents affect the ratio is the same as that given in Table I. *All the condensations except that of o-iodoaniline (vide infra) were* carried out at a temperature between 145° and 150° and the reaction mixture was heated for 3—4 hours.

With regard to the optical rotations of these compounds, (*a*) the *o*-bromo- and *o*-iodo-acids give negative values in acetone and methyl ethyl ketone; (*b*) the *p*-isomeride has in all cases the maximum rotation, which is in accordance with Frankland's rule (J., 1896, **69**, 1583). These observations also support Cohen's rule (Frankland, J., 1912, **101**, 667) "that the rotatory effect of the *ortho-grouping differs more from that of the phenyl than do those* of the meta- and para-groupings"; (*c*) the molecular rotatory powers of the acids do not follow the order of the dielectric constants of the solvents used.

Table II gives the molecular rotatory powers of camphoranilic acid and some of its 2'-substituted derivatives in methyl alcohol, ethyl alcohol, acetone, and methyl ethyl ketone.

As regards their effect in diminishing the molecular rotatory power in acetone and in methyl ethyl ketone, the order of the substituents is that of their effect on the optical activity of menthyl and *sec.*-β-octyl esters of monosubstituted acetic acids and benzoic acids (Rule and Smith, J., 1925, **127**, 2188; Rule and Mitchell, J., 1926, 3202; Rule and collaborators, this vol., p. 178). This

TABLE II.

Substit.	$[M]_D$. MeOH.	EtOH.	Me_2CO.	MeEtCO.
H	+150°	+131°	+101°	—
CO_2H	−584	−574	−551	−390°
Me	+146	+144	+ 98	+ 90·75
I	+ 50·9	—	− 82·8	− 70·17
Br	+ 36·0	+ 21·9	− 61·1	− 31·96
Cl	+ 57·8	+ 35·6	− 40·3	− 28·5
OMe *	+ 29·6	+ 27·6	− 16·3	− 9·55

* Private communication.

corresponds to the relative polarity of the groups as deduced from molecular inductive capacities. For methyl- and ethyl-alcoholic solutions there is a small displacement in the order of the substituents.

It is remarkable that the above order of substituents is followed *when the solvents are ketones and not when they are alcohols.* The substances examined by Rule and his collaborators (*loc. cit.*) were all liquids and the question of the effect of solvents did not arise. *The authors have not been able to find in the literature* mention of any series of optically active, ortho-substituted substances examined in ketonic solution with a view to correlating the molecular rotation with the nature of the *o*-substituent. It seems probable that such optically active substances show the same relative changes in rotatory power in ketonic solvents and in the pure state. Work is in progress to determine whether the effect on the optical activity of substituents in the ortho-position follows the above order only when the substances are dissolved in ketones.

For the meta- and the para-substituted derivatives the effect of the substituents accords with what Rule and others (*loc. cit.*) have called their general effect, *i.e.*, $CO_2H>$halogens$>Me>H$.

EXPERIMENTAL.

Condensation of Camphoric Anhydride with Bromo- and Iodo-anilines.—The method was that described for the condensation of o-chloroaniline (J., 1927, 1995). Sodium carbonate was used to separate the camphoranilic acid from the imide. They can also be separated by fractional crystallisation from alcohol.

Camphoro-*o*-bromophenylimide crystallised in short needles, m. p. 142° (Wootton, J., 1910, **97**, 415, gives 139—140°) (Found: Br, 23·9. Calc.: Br, 23·85%), and the *m*-bromo-isomeride in silky needles, m. p. 190° (Wootton gives 184—185°) (Found: Br, 23·9%).

2'-Bromocamphoranilic acid crystallised in silky needles, m. p. 168°, $[M]_D$ −61·1° in acetone (Wootton gives m. p. about 78°,

$[M]_D$ – 41·1°) (Found : Br, 22·8; equiv., by titration with NaOH, 353·3. Calc.: Br, 22·6%; equiv., 354). The 3′-bromo-acid crystallised in prisms, m. p. 224° after shrinking at 220° (Wootton, 215—217°) (Found: Br, 22·8%; equiv., 353·4).

4′-*Bromocamphoranilic acid* crystallised in stout needles, m. p. 206—207° (Found: Br, 22·7%; equiv., 352·5), and *camphoro*-p-*bromophenylimide* in prismatic needles, m. p. 182·5° (Found: Br, 23·9%).

The condensation of camphoric anhydride and *o*-iodoaniline was carried out at 115°; at higher temperatures a viscous oil was obtained and the yield of the acid was seriously diminished. The alcoholic solution of the condensation product was precipitated with water, and the acid dissolved by addition of dilute aqueous ammonia. The residue was probably unchanged material containing a small quantity of camphoro-*o*-iodophenylimide, which could not be separated and purified. The ammoniacal solution was acidified, yielding an amorphous spongy mass, which was redissolved and reprecipitated several times. 2′-*Iodocamphoranilic acid* was thus

TABLE III.

Rotations of Bromo- and Iodo-camphoranilic Acids and Camphoro-bromo- and -iodo-phenylimides (l = 2).

Temp. 33° (25° for values marked *).

Camphoranilic Acids.

Solvent.	Conc. (g./25 c.c.).	$[\alpha]_D$.	Conc. (g./25 c.c.).	$[\alpha]_D$.	Conc. (g./25 c.c.).	$[\alpha]_D$.
	2′-Bromo-.		3′-Bromo-.		4′-Bromo-.	
MeOH	0·2823	+10·18°	0·3046	+44·3°	0·2654	+51·3°
EtOH	0·2820	+ 6·2	0·2870	+37·7	0·2806	+46·7
Me_2CO	0·3029	–17·3	0·2902	+31·4	0·2776	+35·4
MeEtCO	0·3043	– 9·03	0·3067	+37·4	0·3012	+42·3
	2′-Iodo-.		3′-Iodo-.		4′-Iodo-.	
MeOH	0·2660	+12·7°*	0·2788	+41·69°	0·2887	+44·16°
EtOH	—	—	0·2950	+35·60	0·1954	+42·20*
Me_2CO	0·3539	–20·2*	0·2906	+29·60	0·3061	+36·30
MeEtCO	0·1849	–17·5*	0·3008	+31·60	0·3015	+41·80

Camphorohalogenophenylimides.

	o-Bromo-.		*m*-Bromo-.		*p*-Bromo-.	
MeOH	0·2616	+15·77°	0·3036	+17·70°	0·3056	+15·5°
EtOH	0·2669	+13·37*	—	—	—	—
Me_2CO	0·2858	+ 9·26	0·3012	+14·10	0·2826	+15·87
MeEtCO	0·2906	+10·70	0·3048	+ 9·84	0·2998	+16·67
			m-Iodo-.		*p*-Iodo-.	
MeOH			0·2570	+15·56°	0·2810	+10·67°
EtOH			0·2606	+21·58	—	—
Me_2CO			0·3045	+10·2	0·2853	+ 7·88
MeEtCO			0·3054	+12·27	0·2996	+ 9·59

obtained as a somewhat sticky powder, which was dried in a vacuum desiccator for 48 hours; m. p. 147—149° (Found : I, 31·2 ; equiv., 400. $C_{16}H_{20}O_3NI$ requires I, 31·7% ; equiv., 401).

Camphoro-m-*iodophenylimide* crystallised as a light fluffy mass, m. p. 172° (Found : I, 33·0. $C_{16}H_{18}O_2NI$ requires I, 33·2%), and 3′-*iodocamphoranilic acid* in light prismatic needles, m. p. 226—227° (Found : I, 31·7% ; equiv., 402, 406).

Camphoro-p-*iodophenylimide* crystallised in needles, m. p. 197° (Found: I, 33·1%), and 4′-*iodocamphoranilic acid* in short needles, m. p. 221° (Found : I, 31·8% ; equiv., 399).

In general, the preceding imides are readily soluble in acetone and methyl ethyl ketone, fairly readily soluble in methyl alcohol, and sparingly soluble in ethyl alcohol, and the acids are soluble in the common organic solvents.

4′-Methylcamphoranilic acid (compare Wootton, *loc. cit.*; Singh and Puri, J., 1926, 504) and only a trace of the imide were obtained by the general method.

The rotatory power of 2′-methoxycamphoranilic acid was determined in methyl ethyl ketone for comparison : 0·1989 g. dissolved in 25 c.c. gave $\alpha_D - 0·50°$, whence $[M]_D - 90·75°$.

The authors wish to express their indebtedness to Professor H. B. Dunnicliff for his interest and advice in this work.

GOVERNMENT COLLEGE, PUNJAB UNIVERSITY,
LAHORE (INDIA). [*Received, May 14th,* 1928.]

CCCXXI.—*Studies in the Nitration of Substituted Tertiary Aromatic Amines.*

By GEORGE ROGER CLEMO and JAMES MUIR SMITH.

ALTHOUGH the literature contains a great number of papers on the subject of nitration, this major reaction is still imperfectly understood. The preliminary experiments which led to this investigation were carried out several years ago by one of us (G. R. C.) and C. M. McLeod, but at the time it was not possible to pursue the subject. It has been pointed out by, amongst others, Noelting and Collin (*Ber.*, 1884, **17**, 261) and Pinnow (*Ber.*, 1894, **27**, 3161), that the products of the nitration of certain aniline derivatives vary with the amount of concentrated sulphuric acid used to dissolve the base.

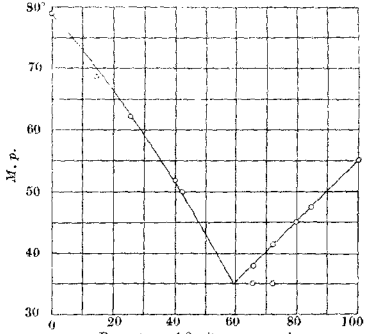
It has now been found that variation of the strength of the sulphuric acid used as the medium for the nitration has in many cases a striking effect on the particular nitro-compound formed.

The experiments of Flürscheim and Holmes on the nitration of benzyldiethylamine (J., 1926, 1562), and of Pollard and Robinson on benzylpiperidine (J., 1927, 2770), which showed that the addition of certain salts to the reaction medium had a marked effect in reducing the proportion of the *m*-nitro-compound formed, are of interest in this connexion.

The bases selected for our experiments were, in the first instance, *p*-chloro-, *p*-bromo-, and *p*-methyl-dimethylaniline, and subsequently more complicated dialkylanilines, including tetramethylbenzidine and 4 : 4′-tetramethyldiaminodiphenylmethane, were employed.

FIG. 1.

Composition–melting point curve for mixtures of 4-chloro-2-nitro- and 4-chloro-3-nitro-dimethylaniline.



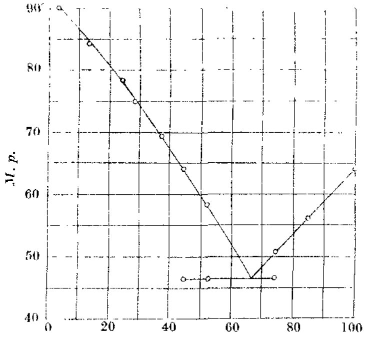
Thus, *p*-chlorodimethylaniline on nitration in concentrated sulphuric acid gives a good yield of the almost pure *m*-nitro-derivative (*Ber.*, 1898, **31**, 2984), whilst in dilute sulphuric acid (75% H_2SO_4 by weight) a good yield of the pure *o*-nitro-compound results—this compound was prepared by Heidlberg (*Ber.*, 1887, **20**, 151) by the action of nitrous acid on the base. With *p*-bromodimethylaniline, approximately parallel results have been obtained, and in both cases the presence of urea inhibits ortho-nitration in dilute sulphuric acid, whilst improving the purity of the *m*-nitro-derivative when concentrated sulphuric acid is used. That the ortho- and meta-nitrations involve essentially different mechanisms for the two reactions is seen also from the fact that, in the latter case, when the

nitration mixture is removed from the cooling bath, the temperature quickly rises some degrees above that of the room, during which time the reaction is completed, whilst, in the former, nitration only occurs with rapid rise of temperature and slight effervescence some 1—4 hours after room temperature has been attained.

It was then decided to submit *p*-chloro- and *p*-bromo-dimethylanilines to a series of nitration experiments in sulphuric acid of various strengths. The analyses of the resulting nitration products were carried out according to the well-known method of Holleman (see Figs. 1 and 2), and, contrary to expectations, it has been found

FIG. 2.

Composition-melting point curve for mixtures of 4-bromo-2-nitro- and 4-bromo-3-nitro-dimethylaniline.



Percentage of 2-nitro-compound.

that the change over from the *o*- to the *m*-nitro-compound is not a gradual process. Thus the chloro-base in sulphuric acid (86% H_2SO_4) gives a product containing 92% of the *o*-compound, whilst in 92% acid a theoretical yield of the *m*-nitro-compound results. With 88 and 90% acid, however, the product is an oil containing both of the nitro-compounds and unchanged base (eutectic temperature of the two nitro-compounds, 35·1°).

The pure materials necessary for the construction of Figs. 1 and 2 were made by the above methods and crystallised from alcohol. The results of the nitrations are summarised in the following tables.

Nitration of 4-Chlorodimethylaniline in Sulphuric Acid of Various Concentrations.

Conc. of H_2SO_4 (% by weight).	Total yield of nitro-compound from 6·2 g. of base.	Proportion of 2- to 3-nitro-compound in product.
50	7·4 g.	95 : 5 *
70	6·5	85 : 15
70 (Urea present)	Nil	—
74·5	6·5	100 : 0
79·4	6·5	100 : 0
83·9	6·3	100 : 0
86·0	5·0	92 : 8
88·3	Oil	Indefinite
90·0	,,	,,
92·0	8·0	9 : 91
93·8	7·5	6 : 94
98·0	7·4	6 : 94
98·0 (Urea present)	7·2	3·5 : 96·5

* All nitrations were effected by the general method described on p. 2420, with the exception of that in 50% sulphuric acid which took two weeks for completion at room temperature.

Nitration of 4-Bromodimethylaniline in Sulphuric Acid of Various Concentrations.

Conc. of H_2SO_4 (% by weight).	Total yield of nitro-compound from 6 g. of base.	Proportion of 2- to 3-nitro-compound in product.
70	7·0 g.	88 : 12
70 (Urea present)	Nil	—
75	5·4	92 : 8
79·4	5·4	97 : 3
83·9	5·5	92 : 8
90·0	3·2	Indefinite
98·0 (Urea present)	7·0	4 : 96

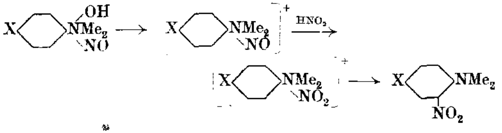
Although no special accuracy is claimed for the figures in column 3 of the above tables, a test in which known amounts of one of the pure isomerides were added to the product of nitration gave composition values from the graph which were within 0·5% of the calculated ones. In marked contrast to the two previous cases, however, *p*-methyldimethylaniline gives a good yield of *o*-nitro-product (*Ber.*, 1895, **28**, 3041; 1897, **30**, 3119) in dilute sulphuric acid in the presence of urea, whilst nitration in concentrated acid gives the normal *m*-nitro-derivative (D.R.-P. 69188; *J. pr. Chem.*, 1902, **65**, 247). It is therefore clear that the nature of the para-substituent plays an important part in ortho-nitration.

Attention was then turned to bases having a para-substituent more powerfully *op*-directing than either Cl, Br, or CH_3, and *p*-dimethylaminobenzyl alcohol was the first selected for study. A difficulty was encountered here, however, as the literature records no suitable method for its preparation (see, however, following paper), and hence a detailed study of its nitration has not yet been carried out. Nevertheless, it has been found in preliminary experi-

ments that this alcohol undergoes nitration in 70% sulphuric acid in presence of urea so readily that the reaction is difficult to control at $-5°$. The benzoyl derivative of *p*-dimethylaminobenzyl alcohol, on the other hand, is recovered largely unchanged under these conditions. Tetramethylbenzidine readily undergoes ortho-nitration in 70% sulphuric acid in the presence of urea (*Ber.*, 1881, **14**, 2164; J., 1926, 2712), whilst in concentrated sulphuric acid meta-nitration proceeds equally easily (*Ber.*, 1904, **37**, 29), and parallel results are obtained with 4:4′-tetramethyldiaminodiphenylmethane (*Ber.*, 1894, **27**, 3161).

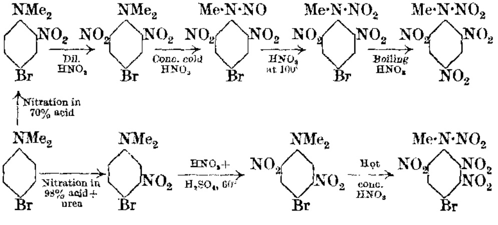
The explanation at present accepted for the meta-nitration of bases dissolved in concentrated sulphuric acid is that it is the kation of the ionised ammonium salt, $[R\cdot NMe_2H]^+$, which undergoes nitration. It is somewhat difficult to understand, however, why such a reaction should proceed smoothly in 92% sulphuric acid, but not in 90 or 88% acid, whilst with 86% acid ortho-nitration occurs, involving a different mechanism. The above explanation, if correct, leads to the curious inference that no ammonium ions are present in the 86% acid (H_2SO_4,H_2O corresponds to 84·5% H_2SO_4), since it has been shown for *p*-chloro- and *p*-bromo-dimethylaniline that the meta-nitration is more rapid than the ortho.

The inbibition by urea in the cases of the two bases just mentioned suggests strongly that nitrous acid plays a fundamental part in the nitration process. This contention is supported by the fact that many such nitro-compounds have been prepared by the action of nitrous acid on a dilute acid solution of the para-substituted dialkylaniline (*Ber.*, 1887, **20**, 151, 2460; 1898, **31**, 2982; 1918, **51**, 1036; J., 1926, 1896). In these cases, however, it is usual to obtain considerable quantities of nitrosoamines on account of the partial dealkylation of the tertiary amino-group, and the fact that these products are not formed in the cases under consideration seems to preclude the explanation that ortho-nitration is due solely to the action of nitrous acid. The best explanation which can be offered is that shown by the following scheme, which involves the prior addition of nitrous acid, followed by ionisation to give the ammonium ion, and oxidation of the nitroso- to the nitro-group, which then migrates into an unoccupied ortho-position.



The fact that urea prevents the reaction when X is Cl or Br, but not when it is $\cdot CH_3$, $\cdot CH_2\cdot OH$, $\cdot CH_2\cdot C_6H_4\cdot NMe_2(p)$, or $\cdot C_6H_4\cdot NMe_2(p)$, may be ascribed to the more acid character of the first two bases, as it is probable that urea will not react with concentrations of nitrous acid sufficient to start the process of ortho-nitration for the other (stronger) bases.

Attention was turned finally to the problem of the further nitration of some of the aforementioned mono-ortho- and -meta-nitro-compounds, and it has been found that, generally, a second nitro-group can be introduced into the *m*-nitro-derivative by nitration in sulphuric acid at 60°, and that the same dinitro-compound is formed directly when the base is treated in concentrated sulphuric acid at 60° with 2 mols. of nitric acid. In the case of *p*-bromodimethylaniline, the resulting dinitro-compound has the same melting point as the compound obtained by the bromination of 3 : 6-dinitrodimethylaniline (Forster and Coulson, J., 1922, **121**, 1995), and hence the second nitro-group in all probability occupies the 6-position. The final stage of the reaction is the production of a trinitro-nitroamine as shown below. The further nitration of the *o*-nitro-derivatives also results in the introduction of a second nitro-group in the 6-position, and the end stage in the nitration of 4-bromo-2-nitrodimethylaniline is tetryl, whilst with the corresponding chloro-base the last stage of the above reaction cannot be carried out, for the chlorine atom is not removed by boiling with fuming nitric acid.



EXPERIMENTAL.

The following general method of nitration was used in the experiments recorded in the tables on p. 2417, with the exception that all the nitration mixtures were allowed to stand together over-night at room temperature, before being poured on ice and worked up.

4-Chloro-2-nitrodimethylaniline.—4-Chlorodimethylaniline (6·2 g.;

0·04 mol.) was dissolved in sulphuric acid (20 c.c.; 75% H_2SO_4 by weight*), cooled in an ice-bath, and stirred whilst a mixture of nitric acid (2·9 c.c.; 66% HNO_3) and sulphuric acid (10 c.c.; 75% H_2SO_4) was run in during ½ hour, the temperature meanwhile being kept at 3—5°. The reaction mixture was allowed to warm to room temperature (21°), and then about 4½ hours later a rapid rise of temperature to 35° occurred, whereupon nitration took place with slight effervescence. After the temperature had fallen again, the mixture was poured on ice, neutralised with caustic soda, the red precipitate collected, well washed with water, and dried in a vacuum (6·5 g.; m. p. 56°). The product was crystallised from methyl alcohol, giving 5 g. of red prisms, m. p. 56° (corr.). If urea (2 g.) was added to the above experiment, and the nitration mixture left overnight at room temperature, 5·8 g. of chlorodimethylaniline were recovered unchanged. 4-*Chloro-2-aminodimethylaniline* was obtained as an oil, b. p. 158°/22 mm., by reducing the nitro-compound with iron and hydrochloric acid (Found: N, 16·6. $C_8H_{11}N_2Cl$ requires N, 16·5%); it forms an *acetyl* derivative, colourless plates from ligroin, m. p. 90° (Found: N, 12·9. $C_{10}H_{13}ON_2Cl$ requires N, 13·1%).

4-*Chloro-3-nitrodimethylaniline*.—This compound was prepared by substituting an equal volume of concentrated sulphuric acid for the 75% acid used above, and nitration was completed with slight rise of temperature as soon as the mixture had reached room temperature. The yield from 6·2 g. of 4-chlorodimethylaniline was 7·5 g., which gave yellow needles (7 g.) from methyl alcohol, m. p. 79° (corr.). The same yield of rather purer nitro-compound was formed when urea was present. 4-*Chloro-3-aminodimethylaniline*, obtained by the reduction of the nitro-compound with iron and hydrochloric acid, forms colourless plates from ligroin; m. p. 54° (Found: N, 16·3. $C_8H_{11}N_2Cl$ requires N, 16·5%); this compound, which darkens after a time in air, forms an *acetyl* derivative, colourless prisms, m. p. 97° (Found: N, 13·0. $C_{10}H_{13}ON_2Cl$ requires N, 13·1%).

4-*Bromo-2-nitrodimethylaniline*.—4-Bromodimethylaniline (8 g.; 0·04 mol.), when nitrated as described above for the corresponding chloro-base, gave 7·2 g. of product containing 92% of the 2-nitro-compound, which crystallised from methyl alcohol in orange-coloured prisms, m. p. 64° (*Ber.*, 1887, **20**, 2460) (Found: N, 11·6. Calc. for $C_8H_9O_2N_2Br$: N, 11·4%). In this case reaction set in one hour after the nitration mixture had reached room temperature (21°), but if urea was present nitration was inhibited. 4-*Bromo-2-aminodimethylaniline* was obtained as an oil, b. p. 165°/23 mm., by

* All subsequent acid percentages are by weight.

reduction of the nitro-compound with iron and hydrochloric acid (Found: N, 13·05. $C_8H_{11}N_2Br$ requires N, 13·0%); its *acetyl* derivative formed colourless, glistening prisms from ligroin, m. p. 111° (Found: N, 10·7. $C_{10}H_{13}ON_2Br$ requires N, 10·9%).

4-Bromo-3-nitrodimethylaniline.—Nitration was carried out in the presence of urea as for the corresponding chloro-compound, and the product gave orange-coloured needles from methyl alcohol, m. p. 93·5° (Found: N, 11·5. $C_8H_9O_2N_2Br$ requires N, 11·4%).

3 : 3′-Dinitro-4 : 4′-tetramethyldiaminodiphenylmethane.—4 : 4′-Tetramethyldiaminodiphenylmethane (10·2 g.) and urea (4 g.) were dissolved in sulphuric acid (60 c.c.; 70%), and a mixture of nitric acid (5·8 c.c.; 66%) and sulphuric acid (20 c.c.; 70%) was added at − 5°. After standing for 1 hour at room temperature, the mixture was worked up in the usual way and gave 9·2 g. of red prisms, m. p. 121° after crystallising from acetic acid.

3 : 3′-Dinitrotetramethylbenzidine.—Tetramethylbenzidine (9·6 g.) was nitrated as in the preceding case and gave 7·4 g. of red needles, m. p. 188°, from acetic acid.

4-Bromo-2 : 6-dinitrodimethylaniline.—4-Bromo-2-nitrodimethylaniline (3 g.) was added in portions to nitric acid (35 c.c.; 52% HNO_3), the temperature being maintained meanwhile at 10°, and subsequently raised to 35° for ½ hour. The resulting acid solution was then gradually diluted with water until the dinitro-compound began to separate, and when precipitation was complete the solid was collected and recrystallised from alcohol, giving orange-coloured diamond-shaped plates (1 g.), m. p. 118° (Found: N, 14·2. $C_8H_8O_4N_3Br$ requires N, 14·4%). 4-Bromo-2 : 6-dinitrophenylmethylnitrosoamine (see below) was also isolated from this reaction.

4-Bromo-2 : 6-dinitrophenylmethylnitrosoamine.—4-Bromodimethylaniline (14 g.) was dissolved in sulphuric acid (56 c.c.; 50%) by warming on a water-bath. Water (48 c.c.) was then added, the solution cooled to 12°, and a mixture of nitric acid (80 c.c.; 66% HNO_3) and sulphuric acid (120 c.c.; 96%) added. After a short time a vigorous reaction set in, and the temperature was kept under 40° by cooling; the nitrosoamine then separated as small, pale yellow needles, which were collected and recrystallised from alcohol (18 g.; m. p. 124°) (Found: C, 27·9; H, 1·55; N, 18·7. $C_7H_5O_5N_4Br$ requires C, 27·6; H, 1·6; N, 18·4%).

4-Bromo-2 : 6-dinitromonomethylaniline.—This was prepared as orange-coloured needles, m. p. 104—105°, by refluxing the above nitrosoamine for 6 hours with methyl-alcoholic hydrogen chloride (Found: N, 15·8. $C_7H_6O_4N_3Br$ requires N, 15·2%).

4-Bromo-2 : 6-dinitrophenylmethylnitroamine.—4-Bromo-2 : 6-dinitrophenylmethylnitrosoamine (1 g.) was dissolved in fuming nitric

acid (15 c.c.) and heated on a water-bath for ten minutes. Water was then added, and the precipitated nitroamine collected and recrystallised from alcohol, giving pale yellow needles, m. p. 113—114°; yield 0·8 g. (Found: C, 26·3; H, 1·9. Calc. for $C_7H_5O_6N_4Br$: C, 26·2; H, 1·6%) (Blanksma, *Rec. trav. chim.*, 1902, **21**, 272).

2 : 4 : 6-*Trinitrophenylmethylnitroamine* (*Tetryl*).—4-Bromo-2 : 6-dinitrophenylmethylnitrosoamine (3 g.) was boiled under reflux with fuming nitric acid (25 c.c.) for 5½ hours, and the resulting solution cooled and poured into water. The yellow solid was collected and crystallised from alcohol, 1 g. of diamond-shaped plates being obtained, m. p. 127°, not depressed when mixed with an authentic specimen of tetryl. The compound gave 2 : 4 : 6-trinitroaniline (m. p. 186°) when treated with ammonia.

4-*Bromo*-3 : 6-*dinitrodimethylaniline*.—4-Bromodimethylaniline (6 g.) was dissolved in sulphuric acid (20 c.c.; 96%) at 40°, the solution stirred, and a mixture of nitric acid (4 c.c.; 66%) and concentrated sulphuric acid (10 c.c.) slowly added. The reaction mixture was allowed to stand over-night, then poured on ice, and neutralised with caustic soda. The precipitate consisted of a mixture of the 3-nitro- and the 3 : 6-dinitro-compound, and was separated by dissolving it in concentrated hydrochloric acid and gradually diluting the solution with water, the less basic dinitro-compound being precipitated; it crystallised from alcohol in deep red plates, m. p. 107° (compare Forster and Coulson, J., 1922, **121**, 1995).

4-*Bromo*-2 : 3 : 6-*trinitrophenylmethylnitroamine*.—Fuming nitric acid (20 c.c.) was added all at once to 4-bromo-3-nitrodimethylaniline (3 g.); a vigorous reaction took place, and when it had subsided the solution was heated for ½ hour on a water-bath and then poured on ice with stirring. The resulting yellow solid was collected, extracted with a small volume of alcohol, and the residue recrystallised from alcohol, pale yellow needles being obtained, m. p. 158° (Found: N, 19·2. Calc. for $C_7H_4O_8N_5Br$: N, 19·1%) (compare Forster and Coulson, *loc. cit.*, who, however, give m. p. 165°).

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UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE. [*Received, July 3rd*, 1928.]

CCCXXII.—*The Reduction of* p-*Dimethylaminobenzaldehyde, and the Preparation of* p-*Dimethylaminobenzyl Alcohol.*

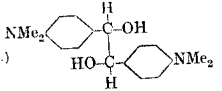
By George Roger Clemo and James Muir Smith.

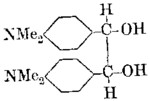
In the course of the experiments described in the preceding paper, *p*-dimethylaminobenzyl alcohol was needed, but it was found that there is some confusion in the literature dealing with this compound, and that no satisfactory method is recorded for its preparation. Thus, Rousset (*Bull. Soc. chim.*, 1894, **11**, 318) claimed to have prepared the alcohol, colourless needles, m. p. 63°, by refluxing the corresponding aldehyde with caustic potash. Braun and Kruber (*Ber.*, 1912, **45**, 2978), however, could not repeat this work, and the present authors have also failed to obtain the alcohol by this means. Geigy and Co. (D.R.-P., 105,105) state that *p*-dimethylaminobenzyl alcohol can be isolated from the action of formaldehyde on dimethylaniline, but Cohn (*Chem.-Ztg.*, 1900, **24**, 564) contradicts the claim. Braun and Kruber, however, uphold Geigy and state that they have thus isolated the alcohol in a 2% yield as an oil which gave an oily benzoyl derivative; a *m*-nitrobenzoyl derivative, m. p. 51°; a methiodide, m. p. 126°; a picrate, m. p. 130°; and a chloroplatinate, m. p. 181°.

Rousset (*loc. cit.*) investigated the reduction of the aldehyde by sodium amalgam in alcohol, but instead of the alcohol obtained a solid, m. p. 155°. It has now been found that this solid is a mixture of two stereoisomeric *s*-*bis*(p-*dimethylaminophenyl*)*ethylene glycols* (I and II), one constituting about two-thirds; and that p-*dimethylaminobenzyl alcohol* can also be isolated from the reaction mixture in a 20% yield of the theoretical. The derivatives of *p*-dimethylaminobenzyl alcohol given by Braun and Kruber do not correspond in a single instance with those now obtained. Thus, it is found that the *benzoyl* derivative has m. p. 91°, the m-*nitrobenzoyl* derivative m. p. 76°, the *methiodide* 232°, and that the *chloroplatinate*, which these authors state to be insoluble in alcohol, crystallises from this medium with solvent of crystallisation, m. p. 100° (decomp.). It has not been found possible to prepare a crystalline picrate from the alcohol, but it is significant (see below) that dimethyl-*p*-toluidine gives a picrate corresponding in properties and m. p. to that given by Braun and Kruber for *p*-dimethylaminobenzyl alcohol.

The action of acids on the stereoisomeric glycols is of a complex nature and the pinacolin transformation has not yet been effected. Further, it has not been possible to prepare acetyl or benzoyl derivatives from (I) and (II). The glycol produced in greater

amount, m. p. 113°, gives a *dimethiodide*, whilst the other, m. p. 178°, under similar conditions, gives only a *monomethiodide*. No resolution experiments, however, have been attempted with a view to settling which glycol has the racemic and which the *meso*-structure.

(I.) 

 (II.)

The electrolytic reduction of *p*-dimethylaminobenzaldehyde has been described by Schepss (*Ber.*, 1913, **46**, 2574), who claims to have thus obtained a 41% yield of *p*-dimethylaminobenzyl alcohol as an oil which solidifies on cooling. It has now been found that in this reduction a mixture of at least the four following compounds is formed: dimethyl-*p*-toluidine, 15% of the theoretical; *p*-dimethylaminobenzyl alcohol, 20%; 4 : 4′-tetramethyldiaminodiphenylmethane; and the glycol, m. p. 178°. In all probability the glycol of m. p. 113° is also formed, but it has not been possible to isolate it from the reaction mixture.

EXPERIMENTAL.

p-*Dimethylaminobenzyl Alcohol.*—*p*-Dimethylaminobenzaldehyde (10 g.) was dissolved in ethyl alcohol (50 c.c.), sodium amalgam (150 g.; 4% Na) added, and the mixture refluxed for 4 hours on the water-bath. The colourless alcoholic solution was decanted into ice and water (250 g.), and the resulting colourless solid (A) was then collected, washed with water, and dried in a vacuum (7·8 g.). The filtrate was saturated with sodium chloride, extracted with ether, and after separation, drying, and fractionation, gave an almost colourless oil (1·6—1·8 g.), b. p. 123°/1 mm. (Found: C, 71·2; H, 8·65; N, 9·4. $C_9H_{13}ON$ requires C, 71·5; H, 8·6; N, 9·3%). p-*Dimethylaminobenzyl alcohol* is somewhat soluble in water, and when treated with benzoyl chloride in presence of caustic soda gives a *benzoate*, colourless prisms from ligroin, m. p. 91° (Found: C, 75·3; H, 6·0; N, 5·7. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7; N, 5·5%). The m-*nitrobenzoate*, on the other hand, can only be prepared by reaction in pyridine, and is obtained as pale yellow plates, m. p. 76°, by crystallising rapidly from ligroin (80°) (Found: C, 64·1; H, 5·6. $C_{16}H_{16}O_4N_2$ requires C, 64·0; H, 5·3%); it is easily soluble in dilute acids, but when its ligroin solution is heated for a short time decomposition occurs. The *methiodide* is easily formed by treating an acetone solution of the alcohol with methyl iodide, and crystallises from ethyl alcohol, in which it is sparingly

soluble, in colourless plates, m. p. 232° (decomp.) (Found: C, 41·4; H, 5·6; I, 43·4. $C_{10}H_{16}ONI$ requires C, 40·9; H, 5·5; I, 43·3%). The *chloroplatinate* forms pale brown leaflets from alcohol, containing solvent of crystallisation, m. p. 100° (decomp.) (Found: Pt, 24·8. $C_{18}H_{28}O_2N_2Cl_6Pt,2C_2H_5{\cdot}OH$ requires Pt, 24·3%).

Solid A. The combined material from three experiments (23·4 g.) was extracted with ether, leaving a solid (8 g.) which crystallised from alcohol in colourless prisms, m. p. 178° (Found: C, 72·1; H, 8·2; N, 9·2. $C_{18}H_{24}O_2N_2$ requires C, 72·0; H, 8·0; N, 9·3%). This *glycol* is sparingly soluble in alcohol, and both its alcoholic and acetic acid solutions show a blue fluorescence, whilst it gives a blood-red solution in sulphuric acid. When a hot acetone solution of the compound is treated with methyl iodide, a *monomethiodide* crystallises, and after recrystallisation from aqueous alcohol (1 : 5) gives colourless prisms, m. p. 232° (decomp.) (Found: C, 51·9; H, 6·3; I, 28·6. $C_{19}H_{27}O_2N_2I$ requires C, 51·7; H, 6·12; I, 28·8%).

On evaporation of the above ethereal extract, a colourless crystalline solid resulted (15 g.), which crystallised from alcohol–ligroin (80°) (1 : 9) in colourless needles, m. p. 113° (Found: C, 72·5; H, 8·0; N, 9·0. $C_{18}H_{24}O_2N_2$ requires C, 72·0; H, 8·0; N, 9·3%). This *glycol* is easily soluble in most organic solvents, giving blue fluorescent solutions. and a blood-red solution in sulphuric acid. When its acetone solution is treated with methyl iodide, the *dimethiodide* separates, which crystallises from alcohol in colourless plates with one molecule of alcohol of crystallisation, m. p. 97° (decomp.) (Found: I, 40·4: 40·0. $C_{20}H_{30}O_2N_2I_2,C_2H_5{\cdot}OH$ requires I, 40·3%).

Electrolytic Reduction of p-*Dimethylaminobenzaldehyde*.—A solution of *p*-dimethylaminobenzaldehyde (10 g.) in sulphuric acid (100 c.c., 20% H_2SO_4) was subjected to a current of 3 amps. in the electrolytic cell described in J., 1918, **113**, 764. The resulting colourless acid solution was made strongly alkaline, extracted with ether, and the extract left over-night, whereupon the glycol, m. p. 178° (0·5 g.), crystallised. When the ether was removed from the filtrate, and the residual oil steam-distilled, an oil rapidly passed over. This was extracted with ether, and the solution dried and fractionated, a colourless, strongly basic oil (1·3 g.) distilling at 70°/1 mm. (*p*-Dimethylaminobenzyl alcohol is but slightly volatile in steam.) The compound forms a picrate, yellow needles from alcohol, m. p. 130°, and a methiodide, colourless prisms from alcohol, m. p. 222°, and the melting points are not depressed when mixed with authentic specimens of the corresponding dimethyl-*p*-toluidine derivatives. The aqueous solution in the steam-distillation flask was decanted from the viscid oil, which was again extracted with water, the combined extract being saturated with sodium chloride and extracted

with ether. On fractionation, *p*-dimethylaminobenzyl alcohol (2·0 g.) passed over at 123°/1 mm. On cooling the viscid oil in ice for some time, a solid crystallised out and was collected and recrystallised from ligroin, forming colourless plates, m. p. 88°, not depressed by admixture with 4 : 4′-tetramethyldiaminodiphenylmethane.

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NEWCASTLE-UPON-TYNE. [*Received, July 3rd,* 1928.]

CCCXXIII.—*Trypanocidal Action and Chemical Constitution. Part VIII. Derivatives of β-Aminoethyl- and γ-Aminopropyl-arsinic Acids.*

By GEORGE ALECK CROCKER GOUGH and HAROLD KING.

THE great success which has attended the treatment of diseases of protozoal and allied origin with aromatic arsenic compounds arose essentially from Ehrlich's discovery that trypanocidally active atoxyl contains arsenic directly linked to the aromatic nucleus, and is, in fact, *p*-aminophenylarsinic acid. From this starting point many aromatic arsenic compounds may be readily synthesised, and since these often show the active properties of the parent substance in an enhanced degree, the attention of chemists and pharmacologists has been directed almost exclusively to this type of compound. In the aliphatic series, the position is quite different. Apart from the work of the early pioneers, which had no primary therapeutic aim, only two important attempts have been made to develop this field—one by the French firm of Poulenc Frères and the other by R. Adams and his co-workers in America. The position, however, is still unsatisfactory, since the aliphatic compounds which have been hitherto examined for trypanocidal action are without the amphoteric characteristics which so often accompany activity in the aromatic series. Thus it is important that any new investigation in this field should include the synthesis of a series of amino-aliphatic arsinic acids, which, by reason of their small molecular weight and their similarity to the amino-acids derived from the tissues, should possess a greater power of penetration and a more favourable distribution. It was therefore decided to prepare a series of compounds of the general type $R_1R_2N{\cdot}[CH_2]_n{\cdot}AsO_3H_2$, where R_1 and R_2 are hydrogen, aliphatic, or alicyclic radicals. Two methods of synthesis of such compounds suggest themselves : (*a*) the action of sodium arsenite on chloroamines of the type $R_1R_2N{\cdot}[CH_2]_n{\cdot}Cl$ (Meyer's reaction), and (*b*) the action of amines on chloro-acids of the type $Cl{\cdot}[CH_2]_n{\cdot}AsO_3H_2$. Since no acids of the latter type have been described, an initial examination of the first method was made,

but the use of β-chloroethyldiethylamine, $CH_2Cl{\cdot}CH_2{\cdot}NEt_2$, β-bromoethyldiethylamine, and *methyl-β-chloroethyldiethylammonium chloride*, $[CH_2Cl{\cdot}CH_2{\cdot}NMeEt_2]Cl$, under various conditions, gave no indication of the formation of arsinic acids. It occurred to us, however, in view of the similarity between *p*-toluenesulphonic esters of aliphatic alcohols and the corresponding halide esters, exemplified from several aspects by Ferns and Lapworth (J., 1912, **101**, 285; compare Kenyon, Phillips, and Turley, J., 1925, **127**, 405) and by Clemo and Walton's extension (this vol., p. 723) of their use to the Friedel–Crafts reaction, that the reactivity of aliphatic toluenesulphonic esters might be applied to the preparation of aliphatic arsinic acids by treatment with sodium arsenite. Such indeed has proved to be the case, for methyl *p*-toluenesulphonate and sodium arsenite give a small yield of methylarsinic acid. In order to extend the scope of the reaction to two cases in which we were interested, an attempt was made to prepare the *p*-toluenesulphonyl ester of diethylaminoethanol and the mono-ester from trimethyleneglycol. In the first case the only product isolated was *tetraethylpiperazinium di-*p*-toluenesulphonate*,

$$\left[\begin{matrix}Et\\Et\end{matrix}{>}N{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}N{<}\begin{matrix}Et\\Et\end{matrix}\right](C_7H_7SO_3)_2,$$

characterised as its *di-iodide* and *dichloroaurate*, products which were identical with those prepared from the product of the polymerisation of β-chloroethyldiethylamine. In the second case the chief products were *trimethyleneglycol di-*p*-toluenesulphonate* and *propane-αγ-dipyridinium di-*p*-toluenesulphonate*,

$$[C_5H_5N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C_5H_5N](C_7H_7SO_3)_2,$$

the latter being characterised as its *dichloride*, *dichloroaurate*, *tetramercurichloride*, and *dipicrate*. Meanwhile, further examination of this extension of the Meyer reaction has been postponed, as the synthesis of the required arsinic acids by method (*b*) has given the desired products.

This alternative method of preparation raised the problem of the synthesis of the chloro-aliphatic arsinic acids. By the interaction of ethylene and arsenious chloride in the presence of aluminium chloride, Renshaw and Ware (*J. Amer. Chem. Soc.*, 1925, **47**, 2991) prepared β-chloroethyldichloroarsine, $CH_2Cl{\cdot}CH_2{\cdot}AsCl_2$. The yield obtained by following their directions is poor and the method, although capable of improvement, was not found convenient for our purpose. As an alternative method, and one which would give access to the higher homologues, the synthesis of hydroxyalkylarsinic acids of the type $CH_2OH{\cdot}[CH_2]_n{\cdot}AsO_3H_2$ was investigated. β-Hydroxyethylarsinic acid has been prepared by the action of sodium arsenite on ethylenechlorohydrin (Poulenc Frères,

B.P. 191028, 1922; Edee, *J. Amer. Chem. Soc.*, 1928, **50**, 1394) and the reaction is also applicable to the preparation of ***γ-hydroxypropylarsinic acid***. When these syrupy acids were dissolved in concentrated hydrochloric acid and reduced with sulphur dioxide in presence of hydrogen iodide, yellow oils separated which, when allowed to react with a petroleum solution of thionyl chloride, gave β-chloroethyldichloroarsine and γ-chloropropyldichloroarsine, respectively. The intermediate yellow oils were purified for chemical examination by distillation at 0·02 mm., and were then found to be the complex arsenious esters resulting from the intermolecular condensation of the primarily formed hydroxyalkyldichloroarsines. In particular, the di-ester of *γ-hydroxypropyldichloroarsine* and *γ-hydroxypropylarsinous acid* was obtained pure,

$$OH{\cdot}C_3H_6{\cdot}As{<}{\begin{matrix}O{\cdot}C_3H_6{\cdot}AsCl_2\\O{\cdot}C_3H_6{\cdot}AsCl_2\end{matrix}}\,.$$

The higher-boiling fractions, which could not be purified, were found to contain an even larger proportion of arsenic to chlorine, and thus were probably still more highly condensed compounds of the general formula $H(OC_3H_6As)_{2n-1}Cl_{2n}$, where n is the number of times that the condensation has been effected (*e.g.*, in the above case, 2; in the compound containing 7 arsenic atoms, 3). Analysis of a sample of the freshly-prepared oil, which had not been subjected to any heat treatment, showed that the first stage of the condensation had already taken place to a large extent.

The interaction of γ-chloropropylarsinic acid and aliphatic or alicyclic amines proceeds normally to yield the corresponding substituted aminopropylarsinic acids. In this way, the arsinic acids produced by the action of ammonia, di- and tri-methylamine, *n*-propylamine, *n*-hexylamine, piperidine, 2 : 2 : *6-trimethylpiperidine*, 3-carbethoxypiperidine, 4-hydroxy-2 : 2 : 6-trimethylpiperidine, *l*-α-phenylethylamine, and piperazine were prepared, and from these a number of substitution products. Owing to the extreme solubility of these simple arsinic acids or their hydrochlorides in water, their isolation has proved a difficult problem, but almost all have been obtained crystalline by the use of appropriate organic solvents. A common impurity which complicated the isolation is probably the corresponding non-crystalline γ-hydroxypropylarsinic acid.

The reactions of *β-chloroethylarsinic acid* were found to be in striking contrast to those of its homologue. With an excess of sodium hydroxide, dimethylamine, or any other strong base, the acid decomposes completely, forming ethylene and the corresponding arsenate and hydrochloride of the base. In the case of ammonia, where the reaction was investigated in some detail, the same decom-

position occurred in aqueous and alcoholic solution at the ordinary temperature and at 100°. When, however, ammonia or the amine was added in sufficient amount to maintain the reaction mixture neutral to litmus, normal, and generally exhaustive, substitution took place without the formation of any arsenic acid. Thus, although it was not possible to obtain such amino-acids as β-aminoethylarsinic acid, the completely substituted compounds, *triethylamine-ββ′β″-triarsinic acid*, $N(CH_2{\cdot}CH_2{\cdot}AsO_3H_2)_3$, and *methyldiethylamine-ββ′-diarsinic acid*, $NMe(CH_2{\cdot}CH_2{\cdot}AsO_3H_2)_2$ were easily obtained. In the preparation of the former compound, it was found that the ammonia could be conveniently supplied by conducting the reaction in the presence of aqueous solutions of carbamide, acetamide, or ammonium acetate, which slowly yielded the ammonia by hydrolysis. The reactive character of β-chloroethylarsinic acid is shown by the fact that some of the quaternary compound, *dimethyldiethylammonium chloride ββ′-diarsinic acid*,

$$\left[\begin{matrix}Me\\Me\end{matrix}\!>\!N\!<\!\begin{matrix}CH_2{\cdot}CH_2{\cdot}AsO_3H_2\\CH_2{\cdot}CH_2{\cdot}AsO_3H_2\end{matrix}\right]Cl\,,$$

is formed in the preparation of *β-dimethylaminoethylarsinic acid*. The substituted arsinic acids from trimethylamine, piperidine, and piperazine were also prepared, the last forming the disubstituted piperazine,

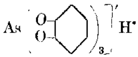
$$AsO_3H_2{\cdot}CH_2{\cdot}CH_2{\cdot}N\!<\!\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}\!>\!N{\cdot}CH_2{\cdot}CH_2{\cdot}AsO_3H_2\,.$$

Whilst β-chloroethyldichloroarsine and γ-chloropropyldichloroarsine are oils, many of the amphoteric arsinic acids of both series (ethyl and propyl) form crystalline dichloroarsine hydrochlorides when sulphur dioxide is passed into a solution of the amphoteric arsinic acid in concentrated hydrochloric acid in the presence of a little hydriodic acid.

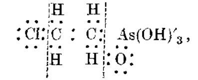
The instability of β-chloroethylarsinic acid towards bases recalls the reactions of β-chlorovinylarsinic acid (Mann and Pope, *J.*, 1922, **121**, 1754), in which acetylene and sodium chloride and arsenate are formed by the action of sodium hydroxide. Since the use of caustic alkali in the hydrolysis of γ-chloropropylarsinic acid yields no arsenic acid, the ease of decomposition must be connected in some way with the presence of the chloro-group in the β-position to the arsinic acid grouping. This particular case of instability may be explained as an example of a general tendency of all arsinic acids. It seems probable that in alkaline solution the arsenic atom in arsinic acids tends to exert a higher co-ordination number than the normal (four), and yields complex ions by combination with one or two hydroxyl ions in which it has an outer electron shell of 10 or 12:

$$[R{\cdot}As{\rightarrow}O(OH)_3]' \text{ and } [R{\cdot}As{\rightarrow}O(OH)_4]''$$

Examples of the formation of stable compounds of a similar type are well known; *e.g.*, tripyrocatechylarsinic acid



(Rosenheim and Plato, *Ber.*, 1925, **58**, 2000). In such complex ions the arsenic–carbon linking will be weakened owing to the drift towards the carbon atom of the electron pair constituting that linking, caused by the negatively charged arsenic atom. If some decomposition can now take place which will result in the loss of two electrons from the alkyl radical (*e.g.*, the removal of a negative ion), then the two electrons forming the arsenic–carbon linking will move into the position between the α- and β-carbon atoms, with the resultant production of a double linking at this point. In the case of β-chloroethylarsinic acid, at this stage the hypothetical co-ordination compound,



consists virtually of intramolecularly ionised ethylene (Lowry, J., 1923, **123**, 822) combined with a chlorine ion and electrically neutral arsenic acid—a system which may easily become arranged into its components when the chlorine ion is removed under the influence of the sodium ions present in the solution. A similar explanation applies to the decomposition of β-chlorovinylarsinic acid.

In the case of γ-chloropropylarsinic acid, although the complex ion may be formed and the chlorine ion removed from it, the electron pair between the arsenic and the α-carbon atoms cannot move along the carbon chain to complete the octet of the terminal carbon atom, since that movement would involve the formation of a ten-electron system around the β-carbon atom. Completion of the γ-carbon octet therefore takes place in the normal way by the addition of a hydroxyl ion, with the consequent formation of γ-hydroxypropylarsinic acid.

Therapeutic Results and Considerations.

Out of more than two dozen compounds described in this communication, all of which contain one of the groups

$$>N{\cdot}CH_2{\cdot}CH_2{\cdot}AsO_3H_2 \text{ or } >N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}AsO_3H_2,$$

only two proved to have any therapeutic activity, and that of a trivial nature, when tested on experimental infections of *Trypanosoma equiperdum* in mice. These were triethylamine-ββ′β″-tri-

arsinic acid, $N(CH_2{\cdot}CH_2{\cdot}AsO_3H_2)_3$, and γ-piperidinopropylarsinic acid, $C_5H_{10}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}AsO_3H_2$. For the former the maximum tolerated dose is 2·5 mg. per g. of mouse, and with a dose of 2·0 mg. the trypanosomes disappear from the peripheral blood of infected mice, but relapse occurs in 6 days; whereas for the latter the tolerated dose is 1·0 mg., and with 0·75 mg. a similar temporary "cure" is followed by relapse in 7 days. The latter compound lends itself to chemical development, but although piperidine was replaced by 2 : 2 : 6-trimethylpiperidine, 3-carbethoxypiperidine, 4-hydroxy-2 : 2 : 6-trimethylpiperidine, and piperazine, and the propyl group by the ethyl group, producing structures of similar build, there was no sign of any therapeutic activity. The results are surprising, for the majority of the compounds prepared and tested were amphoteric and extremely soluble in water—properties which should have ensured a favourable distribution in the mammalian tissues.

In seeking to arrive at some interpretation of this lack of activity, many possibilities arise, but two seem to us to be of predominant importance. Accepting the postulate that the main trypanocidal activity of active arsinic acids is due to their reduction to the corresponding oxides by the tissues, it was pointed out in Part V of this series, where another inactive series was encountered (Hewitt, King, and Murch, J., 1926, 1355; compare also Durham, Marchal, and King, *J. Pharm. Exp. Ther.*, 1926, **28**, 349), that the evidence was all in favour of the view that the inactivity of a series of aromatic arsinic acids containing the sulphonamide group, when compared with their analogously constituted active acids containing the amide group, was due to their non-reduction by the tissues to the corresponding oxides. In other words, these sulphonamide acids lay outside the zone of reduction potential of the tissues. In fact, our view is that variation of the chemotherapeutic index of derivatives of phenylarsinic acid is in part due to the variation in reduction potential produced by various substituents in the *o*-, *m*-, and *p*-positions, just as Conant and Fieser (*J. Amer. Chem. Soc.*, 1924, **46**, 1881) found that the reduction potential of quinones varies with introduction of substituents. All the acids described in this communication contain aliphatically bound arsenic with a chain of at least two methylene groups attached to the arsinic acid, and it may be that such acids are inherently difficult to reduce and that the effect on the reduction potential of wide variation of the remainder of the molecule is lost by the buffering effect of the ethylene or propylene chains.

The other possibility is that these acids are excreted from the system too readily, owing in part to their strikingly great aqueous

solubility, and in part to their lack of substantive properties for the tissues. This substantive effect of efficient medicaments, which keeps them in the body for long periods and allows them to exert a persistent and continuous action, has been emphasised in the case of Bayer 205 and its analogues (Balaban and King, J., 1927, 3078), and it undoubtedly plays an important part in the action of arsenicals (Durham, Marchal, and King, *loc. cit.*). Thus the superior activity of arseno-compounds over arsinic acids, of silver salvarsan over salvarsan, and of zinc sulpharsenol over sulpharsenol, on experimental trypanosome infections in mice, is possibly associated with such longer persistence in the body. The activity of aromatic arsinic acids and the inactivity of aliphatic arsinic acids may be due to an inherently great substantivity of the aromatic nucleus. It may be, on the other hand, that the substantivity of aromatic arsinic acids arises from the fact that, as previously suggested, they come within the zone of reduction potential of the tissues, and are accordingly reduced to the reactive oxides, and stored as such by condensation in a reversible form, whereas the aliphatic arsinic acids are non-substantive because they are outside the reduction potential of the tissues, and cannot therefore be stored as the potentially active oxides.

It is of interest that Castelli (*Arch. Schiff. Trop. Hyg.*, 1912, **16**, 605), working in Ehrlich's laboratory, found mono- and di-methylarsinic acids inactive on experimental trypanosomiasis in mice, a fact confirmed for methylarsinic acid in our laboratories, and that Ritz (*Arch. Internat. Pharmacodyn.*, 1923, **27**, 67) found allylarsinic acid to have no curative action on trypanosome infections in mice. On the other hand, Ritz found that the latter effected a temporary disappearance of *Trypanosoma brucei* in rats, on which methyl- and dimethyl-arsinic acids were inactive, whereas Voegtlin and Smith (*J. Pharm. Exp. Ther.*, 1920, **16**, 449) found methyl- and ethylarsinic acids to possess a definite action on *T. equiperdum* in rats.

We are deeply indebted to Miss F. M. Durham and Miss M. Hill, of this Department, for the painstaking care with which they have carried out the whole of the biological experiments on the toxicities of the individual arsinic acids.

EXPERIMENTAL.

β-*Chloroethylarsinic Acid and Derivatives.*

β-*Hydroxyethylarsinic Acid*, $CH_2OH\cdot CH_2\cdot AsO_3H_2$.—Ethylene chlorohydrin (80 g.) was slowly added to a solution of arsenious oxide (100 g.) and sodium hydroxide (120 g.) in water (300 c.c.) (compare B.P., 191028, 1922; Adams and Quick, *J. Amer. Chem. Soc.*, 1922, **44**, 811; Edee, *ibid.*, 1928, **50**, 1394). The mixture was

cooled and shaken during the addition in order to avoid loss of the chlorohydrin as ethylene oxide. After standing for 12 hours, the whole was warmed on the water-bath for 30 minutes, diluted with water (1500 c.c.), rendered acid with hydrochloric acid (Congo paper), and evaporated until a copious deposit of salt and arsenious oxide had separated. The solid was removed, washed twice with 96% alcohol, the united filtrates evaporated to dryness at 50°, and the residue extracted with alcohol (100 c.c.). On removal of the alcohol, a viscous syrup of crude β-hydroxyethylarsinic acid was left. Contrary to the statement of Edee (*loc. cit.*), this acid on treatment with a hot ammoniacal solution of calcium chloride yields a sparingly soluble *calcium* salt, crystallising from dilute solution in hexagonal leaflets (Found: Loss at 100°, 9·0; Ca, 17·1; As, 32·7, 33·6, 33·7. $C_2H_5O_4AsCa,H_2O$ requires H_2O, 8·0; Ca, 17·7; As, 33·2%).

β-Chloroethyldichloroarsine, $CH_2Cl{\cdot}CH_2{\cdot}AsCl_2$.—Crude β-hydroxyethylarsinic acid, prepared from 100 g. of ethylene chlorohydrin, was dissolved in concentrated hydrochloric acid (350 c.c.), potassium iodide solution (4 c.c. *N*) added, and the solution treated with sulphur dioxide below 50° until saturated. After standing for 48 hours, the lower layer was removed and dried by solution in carbon tetrachloride, followed by removal of the solvent by distillation. The crude oil (140 g.) was then mixed with an equal volume of light petroleum, and thionyl chloride (127 c.c.) added slowly. When the reaction ceased, the product was distilled first at ordinary pressure and finally under reduced pressure. In this manner there were obtained arsenious chloride, b. p. 39—41°/30 mm. (44 g.), and β-chloroethyldichloroarsine, b. p. 92—93°/32 mm. (60 g.). Renshaw and Ware (*J. Amer. Chem. Soc.*, 1925, **47**, 2991) give b. p. 90—93°/30 mm.

In repeating the preparation of β-chloroethyldichloroarsine from ethylene and arsenious chloride by the method of Renshaw and Ware (*loc. cit.*), it was found that the yield of product was very sensitive to slight alterations in the conditions of experiment. In one case in which freshly-distilled arsenious chloride (220 g.) and powdered, freshly sublimed aluminium chloride (29 g.) were treated with ethylene at 0°, an increase in weight of 27 g. was recorded with formation of β-chloroethyldichloroarsine (15 g.). Similar experiments were tried (*a*) with twice the above amount of aluminium chloride, and (*b*) with absorption of the ethylene at 50—60°. Whilst in both these cases a larger increase in the volnme and weight was observed, the yield when the product was worked up by Renshaw and Ware's method was not appreciably altered. It was found, however, that a consistent yield (30 g.) could be obtained by using

the condition (*b*), provided the method of isolation was modified (compare Green and Price, J., 1921, **119**, 449). The reaction mixture was poured into ice-cold 4*N*-hydrochloric acid and evaporated under reduced pressure, the excess of arsenious chloride and the dichloroarsine volatilising without hydrolysis. The last portions of the dichloroarsine (often considerable) may be removed from the tarry residue by distillation in a current of the vapour of 4*N*-hydrochloric acid at 100° and 30 mm. The carbon tetrachloride extract of the total distillate was distilled to remove traces of water, and the residue distilled in a vacuum. The carbon tetrachloride extracts and the arsenious chloride underwent the curious sequence of colour changes noted by Renshaw and Ware; it is of interest that no trace of these coloured compounds was formed in the preparation of β-chloroethyldichloroarsine from β-hydroxyethylarsinic acid.

β-*Chloroethylarsinic Acid*.—Oxidation of the above dichloroarsine with nitric acid, by the method used by Pope and Mann (J., 1922, **121**, 1754) for the corresponding vinyl derivative, caused considerable decomposition: oxidation with chlorine in the presence of water, however, gave the chloro-acid in good yield. β-Chloroethyldichloroarsine (57 g.) was suspended in water (228 c.c.) and dissolved by the passage of chlorine below 50°. On repeated evaporation of this solution with water at 60°, followed by crystallisation of the residue from acetone, β-*chloroethylarsinic acid*, m. p. 134—135° (35 g.), was obtained as pearly plates (Found: As, 39·5. $C_2H_6O_3AsCl$ requires As, 39·8%). The maximum tolerated dose per g. of mouse is 0·2 mg.

Triethylamine-ββ'β''-*triarsinic Acid*.—β-Chloroethylarsinic acid (5 g.) and carbamide (6·3 g.) were heated on the water-bath with sufficient water to render the whole liquid. More water was added from time to time to liberate ammonia by hydrolysis of the carbamide. The reaction was discontinued when a sample contained no un-ionised chlorine (detected by treating a sample with excess of silver nitrate and nitric acid, filtering from silver chloride, and boiling the filtrate with excess of potassium hydroxide to hydrolyse any unreacted chloro-acid; this test was employed throughout the preparations). After excess of carbamide had been removed by extraction with boiling ethyl alcohol (30 c.c.), the residue was dissolved in water (15 c.c.) and made neutral to Congo paper. On cooling, clusters of needles of *triethylamine*-ββ'β''-*triarsinic acid*, m. p. 184—185°, separated (4·1 g.) (Found: As, 47·7; N, 2·7. $C_6H_{18}O_9NAs_3$ requires As, 47·6; N, 2·9%). The acid yields crystalline *calcium* and *barium* salts on treatment in ammoniacal solution with calcium and barium chlorides; the *magnesium* salt is more soluble and is amorphous. The acid is also obtained by the use of acetamide or ammonium acetate as sources of ammonia.

Methyldiethylamine-ββ'-diarsinic Acid.—β-Chloroethylarsinic acid (3 g.) and water (2 c.c.) were heated to 100°, and methylamine (33% aqueous solution) added from time to time to keep the whole neutral. When all the chlorine was ionised (15 hours), the mixture was neutralised with hydrochloric acid (Congo paper), evaporated to dryness, and freed from methylammonium chloride by boiling with ethyl alcohol. The residual gum solidified after prolonged manipulation and was crystallised from a mixture of water and alcohol. *Methyldiethylamine-ββ'-diarsinic acid*, m. p. 192—194°, thus obtained forms rectangular plates (1·9 g.) (*Found*: As, 42·5; N, 3·8; *loss* on heating at 90°, 5·2, 5·1. $C_5H_{15}O_6NAs_2,H_2O$ requires As, 42·5; N, 4·0; H_2O, 5·1%). The maximum tolerated dose is 1·5 mg.

β-Dimethylaminoethylarsinic Acid and *Dimethyldiethylammonium Chloride ββ'-Diarsinic Acid.*—β-Chloroethylarsinic acid (6 g.) was treated with dimethylamine in a similar manner to that employed in the previous preparation. When the reaction was complete (20 hours), the mixture was acidified with hydrochloric acid, evaporated, and freed from dimethylammonium chloride by boiling with chloroform. The residue was dissolved in the minimum volume of water, and alcohol added so long as a precipitate formed. Crystallisation of this precipitate (0·5 g.) from a mixture of alcohol and water yielded compact masses of *dimethyldiethylammonium chloride ββ'-diarsinic acid*, m. p. 178° (Found: N, 3·8; Cl, 9·4. $C_6H_{18}O_6NAs_2Cl$ requires N, 3·8; Cl, 9·2%). The maximum tolerated dose is over 3 mg.

The alcoholic filtrate from the above was concentrated to a small volume (10 c.c.), and acetone (120 c.c.) slowly added. The precipitate, on crystallisation from ethyl alcohol, yielded *β-dimethylaminoethylarsinic acid hydrochloride*, m. p. 138—140° (4·9 g.) (Found: N, 6·0; Cl, 15·2. $C_4H_{12}O_3NAs,HCl$ requires N, 6·0; Cl, 15·2%).

The above quaternary ammonium compound is more readily prepared by the direct interaction of the appropriate reagents. β-Dimethylaminoethylarsinic acid (0·23 g.) and β-chloroethylarsinic acid (0·4 g.) were melted together at 100° by the addition of a few drops of alcohol and heated for 2 days. Solution of the melt in water, followed by the addition of alcohol, yielded the required compound (0·3 g.), identical with that previously prepared.

β-Dimethylaminoethylarsinic Acid Methochloride.—β-Chloroethylarsinic acid (4·9 g.) was treated with trimethylamine according to the method used above. When the reaction was complete, the mixture was dried, the trimethylammonium chloride removed by boiling ethyl alcohol (20 c.c.), and the residue crystallised from methyl alcohol. *β-Dimethylaminoethylarsinic acid methochloride*, m. p. 187—188° (evolution of gas), thus obtained forms elongated

plates (Found: N, 5·7. $C_5H_{16}O_3NAsCl$ requires N, 5·7%). The maximum tolerated dose is less than 0·05 mg.

β-Piperidinoethylarsinic Acid.—β-Chloroethylarsinic acid (7 g.) was dissolved in ethyl alcohol (15 c.c.), and piperidine added until the mixture was neutral to litmus; it was then refluxed, and after 3 hours the reaction again adjusted to neutrality. When interaction had ceased (6 hours), the excess piperidine was removed by basification with sodium hydroxide, followed by evaporation under reduced pressure at 50° until the distillate contained no amine. The residue was made acid with hydrochloric acid, dried, and extracted with boiling ethyl alcohol. Upon concentration of the extract, *β-piperidinoethylarsinic acid hydrochloride*, m. p. 155—157°, separated as lustrous plates (7·5 g.) (Found: Cl, 13·0; N, 5·2. $C_7H_{16}O_3NAs,HCl$ requires Cl, 13·0; N, 5·1%).

For the preparation of the corresponding dichloroarsine, the piperidino-acid (1·5 g.) was dissolved in concentrated hydrochloric acid (4 c.c.) containing a trace of potassium iodide and reduced by passing in sulphur dioxide for 15 mins. The copious precipitate was removed and recrystallised from 2*N*-hydrochloric acid. *β-Piperidinoethyldichloroarsine hydrochloride* thus obtained forms square plates, m. p. 126—127° (evolution of gas), soluble in water and in ethyl alcohol (Found: As, 26·1. $C_7H_{15}NAsCl_3$ requires As, 25·5%). By treatment of this dichloroarsine, dissolved in water (0·9 c.c.), with a saturated aqueous solution of potassium iodide (2·5 c.c.), added drop by drop, bright yellow crystals of *β-piperidinoethyldiiodoarsine hydriodide*, m. p. 158—159°, were obtained (Found: As, 13·1. $C_7H_{15}NAsI_3$ requires As, 13·2%). This substance dissolves in either water or ethyl alcohol with formation of a colourless solution.

NN′-Piperazinedi-ββ′-ethylarsinic Acid.—β-Chloroethylarsinic acid (3 g.) was treated with piperazine hydrate until neutral to litmus, and the resulting mixture heated on the water-bath. The reaction was readjusted to neutrality after 5 hours. A slight trace of un-ionised chlorine persisted after 20 hours' heating. The liquid was concentrated to 10 c.c. and acidified with hydrochloric acid. When the sides of the vessel were rubbed, hexagonal plates of *NN′-piperazinedi-ββ′-ethylarsinic acid dihydrochloride* separated. For analysis and physiological assay, they were recrystallised from 15 c.c. of boiling water; yield, 2·3 g. (Found: As, 32·2; Cl, 15·4. $C_8H_{20}O_6N_2As_2,2HCl$ requires As, 32·4; Cl, 15·3%). This salt is unmelted at 280°, but darkens progressively from 220° upwards. The maximum tolerated dose is 2·5 mg.

β-Chloroethyldiethylamine, $CH_2Cl{\cdot}CH_2{\cdot}N(C_2H_5)_2$, was prepared by a modification of the method given in B.P., 167781 of 1921.

β-Diethylaminoethanol (59 g.), dissolved in chloroform (100 c.c.), was added slowly to a mixture of thionyl chloride (120 g.) and chloroform (500 c.c.) cooled to $-5°$. After standing for an hour, most of the chloroform was removed on the water-bath, and the residue evaporated twice with alcohol under reduced pressure. Crystallisation of the product from alcohol–ether gave stout needles of β chloroethyldiethylamine hydrochloride, m. p. 210—211° (69 g.). Concentration of the mother-liquors gave a further quantity (13 g.). Treatment of the amine hydrochloride (0·5 g.) in water (5 c.c.) with a hot saturated solution of picric acid (0·68 g.) in water yielded the *picrate*, m. p. 116—117°, which crystallised in a compact form from hot solutions, and in needles from cooler solutions. The *chloroaurate*, m. p. 68—71° (somewhat indefinite), crystallises from *N*-hydrochloric acid in hexagonal tablets (Found: Au, 41·1. $C_6H_{14}NCl,HAuCl_4$ requires Au, 41·4%). When the free amine, b. p. 51—52°/16 mm., was kept with an equal volume of absolute alcohol, crystals of 1 : 4-tetraethylpiperazinium dichloride (1 g.) separated, which, when treated with saturated potassium iodide solution (2·5 g. KI), yielded elongated plates of the corresponding di-iodide, identical with that obtained by the interaction of β-diethylaminoethanol and *p*-toluenesulphonyl chloride (see below). No indication of the formation of arsinic acids was obtained by the treatment of β-chloroethyldiethylamine with sodium arsenite under the conditions employed for the preparation of β-hydroxyethylarsinic acid (see above). The amine was largely unattacked, but small amounts of β-diethylaminoethanol and of an unsaturated amine were detected.

Methyl-β-chloroethyldiethylammonium Iodide.—Upon mixing β-chloroethyldiethylamine (26·3 g.) with methyl iodide (3·5 g.) an immediate turbidity was produced and after ½ hour the whole became solid. The excess of methyl iodide was then removed and the residue (51 g.) crystallised from methyl alcohol. *Methyl-β-chloroethyldiethylammonium iodide* thus prepared crystallises in colourless plates, m. p. 219—220°, which are slightly deliquescent and tend to become yellow or red on exposure to air, when wet with solvent (Found: I, 46·1. $C_7H_{17}NClI$ requires I, 45·7%). When treated with sodium hydroxide solution (50%), a concentrated solution of the quaternary salt (80%) yielded an oil, which became solid when the alkali was added in excess. This was found to be the original quaternary iodide liberated unchanged from solution by the "salting out" effect of the sodium hydroxide. Saturated solutions of sodium carbonate and of potassium acetate, but not those of calcium or barium chloride, exert a similar effect.

Methyl-β-chloroethyldiethylammonium chloride was prepared by treating a solution of the iodide (23·5 g.) in water (100 c.c.) with

freshly prepared silver chloride (28 g.) for 20 minutes. The silver iodide was then removed and the liquid stirred with a further quantity of silver chloride (12 g.) for 1 hour to ensure complete conversion. Removal of the water and the silver halides yielded the *chloride* as a mass of highly deliquescent needles, part of which was converted into the *chloroaurate*, m. p. 202—204°, which crystallised from 0·5*N*-hydrochloric acid in fine needles (Found : Au, 40·3. $C_7H_{17}NCl,AuCl_4$ requires Au, 40·3%). No arsinic acid could be isolated by interaction of this chloride and sodium arsenite.

Reaction between Sodium Arsenite and Methyl p-*Toluenesulphonate.*—Methyl *p*-toluenesulphonate (14·2 g.) was stirred at 100° with arsenious oxide (7·2 g.) dissolved in 22 c.c. of 10*N*-sodium hydroxide for 3 hours. When cool, the sodium *p*-toluenesulphonate was removed. and the filtrate treated with just insufficient alcohol to precipitate an oil. On keeping, a small crop of sodium methylarsinate separated in rhombs mixed with fine needles of sodium toluenesulphonate. These could be separated mechanically, and the sodium methylarsinate agreed in all its properties with a specimen prepared from methylarsinic acid. It is, however, preferable to isolate methylarsinic acid as its calcium salt. After removal of sodium toluenesulphonate, the reaction mixture was made slightly acid to Congo paper and evaporated to dryness. On dissolving the residue in water, arsenic trioxide remained undissolved and could be completely eliminated by repetition of the process. Wholly crystalline calcium methylarsinate (1·5 g.) could then be precipitated from a hot ammoniacal solution by excess of calcium chloride. For analysis, the product was dissolved in hydrochloric acid, treated with calcium chloride and reprecipitated from hot dilute solution by excess of ammonia. It then crystallised in microscopic plates (Found : Ca, 20·3. Calc. for CH_3O_3AsCa,H_2O : Ca, 20·5%) having the formula given by Klinger and Kreutz (*Annalen*, 1888, **249**, 152).

Interaction of p-*Toluenesulphonyl Chloride and* β-*Diethylaminoethanol.*—Dry diethylaminoethanol (5·8 g.) was treated with a solution of *p*-toluenesnlphonyl chloride (9·5 g.) in benzene (30 c.c.) at 0°. After standing over-night, the solid which had separated was removed and crystallised from ethyl alcohol. In this way there were obtained elongated, hexagonal plates of *tetraethylpiperazinium di*-p-*toluenesulphonate,* m. p. 300—301° (decomp.) (Found : N, 5·4. $C_{26}H_{42}O_6N_2S_2$ requires N, 5·2%). Upon treatment of this salt (1 g.) with a saturated solution of potassium iodide (2·5 g.) in water, long needles of the corresponding *di-iodide*, unmelted at 300°, separated (Found : I, 55·7; N, 6·1. $C_{12}H_{28}N_2I_2$ requires I, 56·9; N, 6·2%). Treatment of the di-*p*-toluenesulphonate (0·1 g.), dissolved in hot 2*N*-hydrochloric acid (40 c.c.), with auric chloride

gave large, square plates of *tetraethylpiperazinium dichloroaurate* (Found: Au, 45·0. $C_{12}H_{28}N_2Au_2Cl_8$ requires Au, 44·9%). Both this substance and the iodide were found to be identical with the corresponding derivatives prepared from the tetraethylpiperazinium dichloride (see above) formed by the polymerisation of free β-chloroethyldiethylamine. The specimen of the chloroaurate prepared in this way gave similar figures on analysis (Found: Au, 44·9%).

γ-Chloropropylarsinic Acid and Derivatives.

γ-Trimethylene Chlorohydrin.—Preparation of the chlorohydrin from trimethylene glycol and hydrochloric acid by the method of Hultman, Davis, and Clarke (*J. Amer. Chem. Soc.*, 1921, **43**, 369) was found not as satisfactory as the following process based on the method used by Carius (*Annalen*, 1862, **124**, 257) for the preparation of ethylene chlorohydrin: Sulphur monochloride (2200 g.) was added with vigorous stirring to trimethylene glycol (1000 g.) heated to 70°, at such a rate that the evolved gases could be easily absorbed. After stirring for a further 2 hours, the mixture was cooled and filtered from suspended sulphur. Distillation of the filtrate yielded impure trimethylene dichloride (40 g.) and trimethylene chlorohydrin, b. p. 74—76°/23 mm. (850 g.).

γ-Hydroxypropylarsinic Acid.—Trimethylene chlorohydrin (95 g.) was stirred with sodium arsenite solution (100 g. As_2O_3 and 120 g. NaOH dissolved in 300 c.c. of water) at 50—60° until homogeneous. The liquid was then diluted with an equal volume of water, neutralised to Congo paper, and evaporated to dryness at 50°. Extraction of the residue with hot alcohol (150 c.c.) yielded, after removal of the alcohol, a syrup of impure *γ-hydroxypropylarsinic acid*. This acid yields a crystalline *calcium* salt (Found: As, 33·2. $C_3H_7O_4AsCa$ requires As, 33·8%).

γ-Chloropropyldichloroarsine.—γ-Hydroxypropylarsinic acid (from 95 g. of trimethylene chlorohydrin) was dissolved in concentrated hydrochloric acid (250 c.c.), containing potassium iodide (0·3 g.), and sulphur dioxide passed to saturation, the temperature being kept below 40°. After standing for 2 days, the lower layer (85 g.) was separated and dried by distilling carbon tetrachloride from it. It was then mixed with light petroleum (90 c.c.), and thionyl chloride (56 c.c.) added with cooling and agitation. After refluxing for 2 hours, the petroleum was removed and the residue distilled. In this manner there were obtained arsenious chloride, b. p. 45°/32 mm. (13 g.), and *γ-chloropropyldichloroarsine*, b. p. 120—122°/16 mm. (70 g.) (Found: As, 33·5. $C_3H_6AsCl_3$ requires As, 33·6%).

γ-Chloropropylarsinic Acid.—Chlorine was passed into a suspension of γ-chloropropyldichloroarsine (40 g.) in water (160 g.) until solution

was complete. By repeated evaporation of the solution with water, followed by crystallisation of the residue from water, elongated hexagonal plates of *γ-chloropropylarsinic acid*, m. p. 146—148°, were obtained (Found: As, 37·1. $C_3H_8O_3AsCl$ requires As, 37·0%). This acid yields crystalline *barium* and *calcium* salts with ammoniacal barium and calcium chlorides. The maximum tolerated dose is 0·1 mg.

The Reaction between γ-Hydroxypropylarsinic Acid and Sulphur Dioxide.—The oil which separated when the hydroxy-acid was treated with sulphur dioxide in hydrochloric acid solution was dried as already described. Complete decomposition occurred at 140° when the oil was heated at 15 mm.; at 0·15 mm., however, there was little decomposition and the crude product (15 g.) gave a very volatile substance (arsenious chloride), a light yellow, mobile liquid, b. p. 34—35° (8·5 g.), a darker liquid, b. p. 35—75°, and a residue (5·2 g.). The second fraction was redistilled, b. p. 35°/0·16 mm., and left only a minute residue. Analysis showed it to be the *di-ester* of *γ-hydroxypropyldichloroarsine* and *γ-hydroxypropylarsinous acid*, $(AsCl_2{\cdot}C_3H_6{\cdot}O)_2As{\cdot}C_3H_6{\cdot}OH$ (Found: As, 41·3; Cl, 26·6. $C_9H_{19}O_3As_3Cl_4$ requires As, 41·5; Cl, 26·2. γ-Hydroxypropyldichloroarsine, $C_3H_7OAsCl_2$, requires As, 36·6; Cl, 34·6%). The third fraction and the residue appeared to contain small amounts of more complex condensation compounds (Found: In the third fraction, As, 41·3; in the residue, As, 42·3%). The ester, b. p. 35°/0·16 mm. (10 g.), on treatment with thionyl chloride (8 c.c.) at 0° yielded finally γ-chloropropyldichloroarsine (4·9 g.).

γ-Aminopropylarsinic Acid.—γ-Chloropropylarsinic acid (7 g.) was found to react completely with ammonia (*d* 0·88; 50 c.c.) without the production of arsenic acid, when heated at 110° for 8 hours. After the excess of free ammonia had been removed by warming under reduced pressure, the product was made alkaline with sodium hydroxide and distilled at 50° until the distillate was neutral. The residue was then made acid (Congo paper) with hydrochloric acid, evaporated to dryness, and the organic matter separated from the salt by extraction with alcohol. After removal of the alcohol, the residue was dissolved in water, neutralised to litmus paper with sodium hydroxide, evaporated to dryness, and extracted with pure methyl alcohol. Gradual addition of acetone to the extract yielded the amino-acid which was now sparingly soluble in methyl alcohol. It was freed from a trace of a substance containing ionic chlorine by boiling with a little methyl alcohol. *γ-Aminopropylarsinic acid*, m. p. 212—214° (evolution of gas), obtained in this way, forms compact, microscopic prisms which are extremely soluble in water, but insoluble in ethyl alcohol (Found: N, 7·5. $C_3H_{10}O_3NAs$ requires N, 7·6%). The maximum tolerated dose is 0·4 mg.

γ-Dimethylaminopropylarsinic Acid.—γ-Chloropropylarsinic acid (6 g.) was heated with a methyl-alcoholic solution of dimethylamine (6 c.c. of 33%) at 110° for 8 hours and the excess of amine removed by distillation with sodium hydroxide solution under reduced pressure. The residue was acidified with hydrochloric acid, evaporated to dryness at 50°, and extracted with alcohol. Gradual addition of acetone to this gave a precipitate, which was removed and recrystallised from ethyl alcohol (6 c.c.). *γ-Dimethylaminopropylarsinic acid hydrochloride*, m. p. 108—110°, thus obtained forms slightly deliquescent needles (Found: Cl, 14·4; N, 5·7; As, 30·4. $C_5H_{14}O_3NAs,HCl$ requires Cl, 14·3; N, 5·7; As, 30·3%). The maximum tolerated dose is 0·4 mg.

γ-Dimethylaminopropylarsinic Acid Methochloride.—The chloro-acid (6 g.) was heated with trimethylamine (30 c.c. of 33% aqueous solution) at 100°. After 3 hours the water and excess of amine were removed and the residue extracted with chloroform (30 c.c.) to remove trimethylammonium chloride. The residue, which solidified on being kept for 2 days, was dissolved in the minimum volume of water at 70°, and ethyl alcohol added at that temperature until a turbidity was produced. On cooling, compact prisms of *γ-dimethylaminopropylarsinic acid methochloride* separated, m. p. 174—176° (Found: Cl, 13·5; N, 5·4. $C_6H_{17}O_3NAsCl$ requires Cl, 13·6; N, 5·4%), which did not yield a sparingly soluble picrate or chloroaurate. The maximum tolerated dose is 0·3 mg.

*γ-*n*-Propylaminopropylarsinic Acid.*—γ-Chloropropylarsinic acid (6 g.) was refluxed with alcohol (40 c.c.) and *n*-propylamine (10 g.; 6 mols.) for 12 hours. When the reaction was complete, the excess amine and alcohol were removed, first by distillation alone and then with sodium hydroxide under reduced pressure. The residue, when acidified with hydrochloric acid, dried, and extracted with alcohol, yielded *γ-*n*-propylaminopropylarsinic acid hydrochloride*, m. p. 210—212° (Found: As, 28·2; N, 5·3; Cl, 13·6. $C_6H_{16}O_3NAs,HCl$ requires As, 28·6; N, 5·4; Cl, 13·6%). The maximum tolerated dose is 0·5 mg. The acid, prepared by treatment of the hydrochloride (0·47 g.) with sodium hydroxide (1 mol.) followed by evaporation to dryness, was extracted from the residue with methyl alcohol (2 c.c.); on addition of ethyl alcohol (12 c.c.), in which it is insoluble, needles of *γ-*n*-propylaminopropylarsinic acid*, m. p. 222—224°, slowly separated (Found: N, 6·1. $C_6H_{16}O_3NAs$ requires N, 6·2%). The acid is neutral to litmus, and yields a white, basic arseno-compound on warming with hypophosphorous acid containing a trace of potassium iodide.

m-Nitrobenzopropylamidopropylarsinic Acid.—γ-*n*-Propylaminopropylarsinic acid hydrochloride (1·5 g.), dissolved in 2*N*-sodium

hydroxide (9 c.c.), was shaken with powdered *m*-nitrobenzoy chloride (1·45 g.). After 10 minutes equal additional quantitie of the latter two reagents were introduced. After further shaking the mixture was acidified with hydrochloric acid and the resultan system of oil, solid, and water extracted thrice with ether. Th oil and the aqueous portion were then evaporated to dryness an extracted with ethyl alcohol. Evaporation of the alcohol left a oil which crystallised after long contact with ethyl acetate. Crystal lisation of this solid from aqueous alcohol yielded m-*nitrobenzo propylamidopropylarsinic acid*, m. p. 132—134° (Found: As, 19·9 $C_{13}H_{19}O_6N_2As$ requires As, 20·0%). The corresponding *benzoy* compound is an oil which could not be crystallised.

γ-n-*Propylaminopropyldichloroarsine Hydrochloride*.—A solution o the amino-acid hydrochloride (1 g.) in concentrated hydrochlori acid (4 c.c.) containing a trace of potassium iodide was treated wit sulphur dioxide until saturated. The crystals which separated o chilling were removed and recrystallised from concentrated hydro chloric acid (5 c.c.) with sufficient water to complete solution at th boiling point. γ-n-*Propylaminopropyldichloroarsine hydrochloride* m. p. 195—196°, thus obtained forms elongated hexagonal tablets which rapidly reduce a solution of iodine in potassium iodide and yield a yellow solid on treatment with saturated potassium iodide solution (Found: As, 26·4. $C_6H_{14}NAsCl_2,HCl$ requires As, 26·6%). The maximum tolerated dose is 0·0075 mg. It rendered trypanosomes non-infective at a dilution of 1 : 40,000 in horse-serum after 4·5 hours' contact.

γ-n-*Hexylaminopropylarsinic Acid*.—The chloro-acid (6 g.) and *n*-hexylamine (18 g.) were heated at 100° for 20 hours. After removal of the excess of amine, by distillation first under reduced pressure and then in the presence of sodium hydroxide, the residue was acidified with hydrochloric acid, evaporated to dryness, and extracted with ethyl alcohol (15 c.c.). The crystalline product, obtained by cooling the extract in ice, was recrystallised from ethyl alcohol and then yielded short, flat plates of γ-n-*hexylaminopropylarsinic acid hydrochloride*, m. p. 221—223° (6·2 g.). The maximum tolerated dose is 0·025 mg. The m-*nitrobenzoyl* derivative, m. p. 118—120°, prepared from the amino-acid hydrochloride (3·5 g.), *m*-nitrobenzoyl chloride (4·4 g.), and 2*N*-sodium hydroxide (35 c.c.) by the method already described, formed white plates (Found: As, 18·4. $C_{16}H_{25}O_6N_2As$ requires As, 18·0%). The maximum tolerated dose is less than 0·025 mg. The corresponding m-*amino-benzoyl* compound, formed by reduction with ferrous hydroxide, could not be obtained in a crystalline state either free or as the hydrochloride.

γ-Carbethoxy-n-*hexylaminopropylarsinic Acid.*—Ethyl chloroformate (1·2 g.) was added in small amounts with vigorous stirring to an ice-cold solution of the amino-acid (1 g.) in *N*-sodium hydroxide (6 c.c.). When the odour of the chloroformate had disappeared, the solution was acidified with hydrochloric acid and the precipitated oil removed. After prolonged manipulation and keeping at −5°, this solidified and was crystallised from ether–light petroleum. *γ-Carbethoxy*-n-*hexylaminopropylarsinic acid*, m. p. 58—60°, thus obtained, formed long, flat plates (Found: N, 4·1. $C_{12}H_{26}O_5NAs$ requires N, 4·1%). The maximum tolerated dose is 0·005 mg.

γ-Phenylcarbamyl-n-*hexylaminopropylarsinic Acid.*—Phenylcarbimide (4 g.) was added drop by drop to an ice-cold solution of the amino-acid hydrochloride (3 g.) in *N*-sodium hydroxide (25 c.c.) with vigorous stirring. The diphenylcarbamide that separated was removed and the filtrate made acid (Congo paper). The precipitated oil, which solidified after long keeping at 0°, was crystallised from aqueous alcohol and yielded *γ-phenylcarbamyl*-n-*hexylaminopropylarsinic acid*, m. p. 118—124° (indef.). The maximum tolerated dose is 0·01 mg.

γ-n-*Hexylaminopropyldichloroarsine hydrochloride*, prepared in a similar manner to that employed for the corresponding propyl compound from the amino-acid hydrochloride (3 g.) and concentrated hydrochloric acid (30 c.c.), forms large hexagonal plates, m. p. 190—192°, when crystallised from 2*N*-hydrochloric acid (100 c.c.) (Found: As, 23·1. $C_9H_{20}NAsCl_2$,HCl requires As, 23·1%).

l-*α-Phenylethylaminopropyldichloroarsine Hydrochloride.*—The interaction of *l*-α-phenylethylamine (3·1 g.) and the chloro-acid (1·5 g.) was carried out in a manner similar to that employed for the preparation of the hexylamino-acid. The product, which remained as a glassy gum, could not be obtained pure and was converted directly into the dichloroarsine by treatment with hydrochloric acid and sulphur dioxide. The precipitate was crystallised from 2*N*-hydrochloric acid and the l-*α-phenylethylaminopropyldichloroarsine hydrochloride*, m. p. 194—196°, thus obtained, formed large hexagonal plates (Found: As, 21·9. $C_{11}H_{16}NAsCl_2$,HCl requires As, 21·8%). The maximum tolerated dose is 0·005 mg.

γ-Piperidinopropylarsinic Acid.—A mixture of the chloro-acid (6 g.) and piperidine (26 g.) was heated for 6 hours at 100°, crystals of piperidine hydrochloride being deposited almost immediately. When the chlorine was completely ionised, the excess of free and combined piperidine was removed, the residue acidified with hydrochloric acid, and evaporated to dryness at 50°. The ethyl-alcoholic extract of the residue, when concentrated and chilled, deposited crystals which were recrystallised from boiling alcohol. *γ-Piperidino-*

propylarsinic acid hydrochloride thus obtained (5 g.) formed square plates, m. p. 162—164° (Found : N, 4·8; Cl, 12·4. $C_8H_{18}O_3NAs,HCl$ requires N, 4·9; Cl, 12·3%).

γ-Piperidinopropyldichloroarsine hydrochloride was prepared by treatment of the acid hydrochloride (3 g.), dissolved in concentrated hydrochloric acid (9 c.c.), with sulphur dioxide. The precipitated solid yielded hexagonal plates, m. p. 194—196° (2·4 g.), when crystallised from 4*N*-hydrochloric acid. The maximum tolerated dose is 0·01 mg.

γ-4-Hydroxy-2 : 2 : 6-trimethylpiperidinopropylarsinic Acid.—The chloro-acid (2 g.) was heated with vinyldiacetonealkamine (6·9 g.) and ethyl alcohol (20 c.c.) for 2 days. After basification with sodium hydroxide, followed by evaporation to dryness, the excess of amine was removed by exhaustive extraction with benzene, and the residue dissolved in water and made neutral to methyl-orange. The liquid was then evaporated to dryness and extracted with boiling methyl alcohol. On concentration of the extract, white, microscopic crystals separated. Recrystallisation of these from methyl alcohol yielded deliquescent *γ-4-hydroxy-2 : 2 : 6-trimethylpiperidinopropylarsinic acid*, m. p. 162° (Found : N, 4·7. $C_{11}H_{24}O_4NAs$ requires N, 4·5%). The maximum tolerated dose is 0·2 mg.

γ-2 : 2 : 6-Trimethylpiperidinopropylarsinic Acid and 2 : 2 : 6-Trimethylpiperidine.—4-Bromo-2 : 2 : 6-trimethylpiperidine hydrobromide (44 g.), prepared from vinyldiacetonealkamine by the method of Pauly and Harries (*Ber.*, 1898, **31**, 667), was reduced by heating with glacial acetic acid (240 c.c.) and zinc dust (66 g.) for 6 hours. The solids were then removed and washed with hot acetic acid. The acid was then removed from the combined filtrates by distillation under reduced pressure, and the basified residue distilled in a current of steam until the distillate was neutral. The ethereal extract of the latter distillate yielded 2 : 2 : 6-*trimethylpiperidine*, b. p. 138—139° (20 g.); *hydrochloride*, m. p. 236—237° (Found : Cl, 21·6. $C_8H_{17}N,HCl$ requires Cl, 21·7%). The followiug characteristic colour reactions are given by addition of this and similar amines (0·02 c.c.) to a 0·5% solution of sodium nitroprusside (20 c.c.) containing acetaldehyde (0·02 c.c.) (Lewin, *Ber.*, 1899, **32**, 3388): piperidine, initially violet-blue, unchanged after 4 hours; 2 : 2 : 6-trimethylpiperidine, initially wine-red, finally magenta; 3-carbethoxypiperidine, initially blue, finally green. The *chloroaurate*, prepared by treating a solution of the amine (0·1 g.) in 2*N*-hydrochloric acid (4 c.c.) with aqueous auric chloride until no further turbidity was produced, followed by crystallisation of the oil from *N*-hydrochloric acid, forms octahedra, m. p. 127—129° (Found : Au, 42·0. $C_8H_{17}N,HAuCl_4$ requires Au, 42·2%). The

picrate, prepared by the action of saturated aqueous picric acid on the amine (0·1 g.), followed by crystallisation of the precipitated oil from water, forms well-developed rhombs, m. p. 195—196°. For the preparation of the substituted aminopropylarsinic acid, γ-chloropropylarsinic acid (2·5 g.) was heated on the water-bath with the amine (10 g.) and alcohol (10 c.c.) for 6 hours. The solvent and free amine were then removed by distillation in the presence of sodium hydroxide, and the residue acidified with hydrochloric acid and evaporated to dryness. The ethyl-alcoholic extract of this yielded the amino-acid hydrochloride, which could not be obtained in a crystalline state; it was therefore converted into the free acid by adjusting the reaction to neutrality to litmus, evaporating the water, and extracting the residue with boiling methyl alcohol. Addition of dry ether to this extract yielded deliquescent, microscopic crystals of *γ-2 : 2 : 6-trimethylpiperidinopropylarsinic acid*, m. p. 150—160° (indef.) (Found: N, 4·4. $C_{11}H_{24}O_3NAs$ requires N, 4·8%). The maximum tolerated dose is 2·0 mg.

γ-Piperazinopropylarsinic Acid.—The product obtained by heating the chloro-acid (4 g.) with piperazine hydrate (24 g.) at 100° for 20 hours, was freed from piperazine by distillation in a current of steam at 100° under reduced pressure in the presence of sodium hydroxide. When the distillate no longer gave a precipitate with picric acid, the residue was acidified with hydrochloric acid (Congo paper), dried, and extracted with boiling ethyl alcohol. Upon concentration and cooling of the extract, a thick syrup separated which slowly solidified. Crystallisation of this from ethyl alcohol (30 c.c.) yielded *γ-piperazinopropylarsinic acid dihydrochloride* (Found: Cl, 21·9. $C_7H_{17}O_3N_2As,2HCl$ requires Cl, 21·8%). The maximum tolerated dose is 2·0 mg. The benzoyl derivative was obtained by the Schotten–Baumann method from the amino-acid hydrochloride (3·3 g.), benzoyl chloride (3·0 g.), and 2*N*-sodium hydroxide (35 c.c.). After the benzoic acid had been removed from the acidified reaction mixture by extraction with ether, the residue was evaporated to dryness and extracted with ethyl alcohol. This extract yielded a white solid which, when crystallised from aqueous acetone, yielded *γ-4-benzoylpiperazinopropylarsinic acid*, m. p. 204—206° (decomp., eff.) (Found: N, 8·0. $C_{14}H_{21}O_4N_2As$ requires N, 7·9%). The maximum tolerated dose is 0·2 mg.

γ-3-Carbethoxypiperidinopropylarsinic Acid.—The chloro-acid (3·1 g.) was heated with ethyl nipecotinate (15·7 g.) (prepared from nicotine by the method of Adams and McElvain, *J. Amer. Chem. Soc.*, 1923, **45**, 2745) for 15 hours at 90°. The ethyl nipecotinate was then removed by adding sodium hydroxide (8 c.c.; 40%) to a solution of the product in water (30 c.c.) at 0°, followed by extraction

with ether. The aqueous residue was then made acid with hydrochloric acid (methyl-orange) and evaporated to dryness at 50°. Extraction of this solid with boiling methyl alcohol (20 c.c.), followed by the addition of ethyl alcohol, yielded the desired amino-acid in an impure condition. For analysis and physiological testing, it was dissolved in methyl alcohol (15 c.c.) and poured into dry ether (120 c.c.). *γ-3-Carbethoxypiperidinopropylarsinic acid* thus obtained was dried in a vacuum in the presence of sulphuric acid and sodium hydroxide and ground under dry ether; it then formed an amorphous, deliquescent solid (Found: N, 4·3; As, 22·9. $C_{11}H_{22}O_5NAs$ requires N, 4·3; As 23·2%). The maximum tolerated dose is 1·5 mg.

Interaction of Trimethylene Glycol and p-*Toluenesulphonyl Chloride in the Presence of Pyridine.*

p-Toluenesulphonyl chloride (19 g.) was added in small portions to a mixture of trimethylene glycol (4 g.) and pyridine (8 g.) at 0°. Crystals of pyridine hydrochloride filled the liquid after about ½ hour, but became smaller in bulk after 20 hours, whereupon the whole was treated with water (100 c.c.). The oil which separated was removed and washed twice with dilute hydrochloric acid and with water. Since it possessed a pronounced smell of trimethylene dichloride, it was distilled with water under reduced pressure. By this treatment a small amount of volatile oil was obtained which, when extracted with ether and dried, gave trimethylene dichloride, b. p. 120—122°. The semi-solid residue of the steam distillation, after being dried in a vacuum, was extracted with ether, and the insoluble portion crystallised from methyl alcohol (6 c.c.). It separated in hexagonal plates (2·5 g.) which proved to be *trimethylene glycol di-*p-*toluenesulphonate*, m. p. 93—94° (Found: C, 52·8; H, 5·4. $C_{17}H_{20}O_6S_2$ requires C, 53·1; H, 5·3%). The aqueous extract of the original reaction mixture was freed from pyridine by distillation with sodium hydroxide under reduced pressure, concentrated (to 20 c.c.), and made neutral to litmus with hydrochloric acid; addition of saturated aqueous mercuric chloride solution then yielded a crystalline *mercury* salt, which in turn afforded an amine hydrochloride in the usual way. For examination of the properties of this amine the original reaction was conducted under modified conditions calculated to favour the production of a quaternary compound. Trimethylene glycol (4 g.) and pyridine (8 g.) were mixed with *p*-toluenesulphonyl chloride (19 g.) in a single addition and the reaction was allowed to proceed without cooling. When the reaction had subsided, the mixture was warmed on the water-bath for 2 hours. The crop of large, crystalline plates which separated

cooling was washed with ether to remove pyridine and crystallised ›m acetone (30 c.c.). The deposited crystals (3·1 g.) were free from ıised chlorine and proved to be *propane-αγ-dipyridinium di-oluenesulphonate*, m. p. 118—120° (Found : N, 5·2. $C_{27}H_{30}O_6N_2S_2$ ›uires N, 5·2%). When treated with a saturated aqueous solution mercuric chloride, this substance is converted into the correspond- *mercurichloride*. Crystallisation of the precipitated salt from iling water gave a product from which the mercuric chloride was ınd to have partly dissociated (Found : Cl, 26·1; Hg, 57·5. $H_{16}N_2Cl_2,4HgCl_2$ requires Cl, 26·1; Hg, 59·1%); but crystal-ısation in the presence of an excess of mercuric chloride yielded clusters of radiating needles of the pure mercurichloride (Found : Cl, 26·1; Hg, 59·5%). The combination of four molecules of mercuric chloride with one molecule of a diquaternary compound has been observed previously in a few cases (*e.g.*, Curtius and Clemm, *J. pr. Chem.*, 1900, **62**, 194). For the preparation of the diquaternary dichloride the *mercurichloride* was suspended in warm water and decomposed with hydrogen sulphide in the usual way. Evaporation of the aqueous product to dryness yielded an oil which, when dried in a vacuum, formed a mass of needle-like crystals, and recrystallisation from alcohol–ether gave pure *propane-αγ-dipyridinium dichloride* (Found : Cl, 26·3. $C_{13}H_{16}N_2Cl_2$ requires Cl, 26·1%). Treatment of this salt (0·1 g.) in boiling *N*-hydrochloric acid (40 c.c.) with aqueous auric chloride yielded, on cooling, elongated rectangular plates of the *dichloroaurate*, which became dark yellow when heated and were unmelted at 300°; on cooling, the original light yellow colour is restored (Found : Au, 44·7. $C_{13}H_{16}N_2Au_2Cl_8$ requires Au, 44·9%). The corresponding *dipicrate* crystallises from water in long, stout prisms, m. p. 176°.

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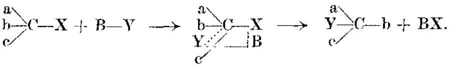
CCCXXIV.—*The Walden Inversion.*

By HANS NICOLAI KELLERMAN RØRDAM.

THE discovery by Walden in 1896 of the stereochemical inversion to which his name is now given raised a problem which still remains unsolved. Since the optical isomerides always possess the same chemical properties, the same energy content, the same solubility, etc., and the corresponding reactions consequently have the same affinities, there is no apparent reason why, for instance, silver oxide and water should transform *l*-chlorosuccinic acid into *l*-malic acid, whilst potassium hydroxide converts it into *d*-malic acid.

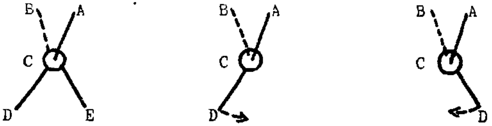
Also, although Senter (J., 1915, **107**, 638 *et seq.*) has shown that tl nature of the solvent can influence the inversion, and Holmbe (*e.g.*, *J. pr. Chem.*, 1913, **87**, 456; **88**, 553) has demonstrated th it is sensitive to the presence of salts and to changes in concentrati of the reagents, yet no mechanism has hitherto been suggest which is capable of explaining all the results or of predicting t occurrence of an inversion.

Holmberg (*Ber.*, 1926, **59**, 125; *Svensk Kem. Tidskr.*, 1927, **39**, has suggested a theory according to which the determining fact for a Walden inversion is to be found in what he has termed " t reaction distance," *i.e.*, the distance between the two reacti parts of the molecule or ion acting upon the optically active coı pound, *e.g.*, the distance between H and OH in a molecule of wat or, in general, between B and Y in the reacting molecule B—Y the reaction:



If the distance B—Y is greater than the distance C—X, then inversion must take place, but if the latter distance is the greater, no inversion will occur. Since, however, the ratio of these two distances must be the same so long as we are considering the same reaction, this hypothesis (unless additional assumptions are made) is inconsistent with the influence exercised upon the inversion by the various factors mentioned above.

By means of the following conception, it is possible to explain the phenomenon and to calculate the fraction *n* of the reaction product which has a steric configuration agreeing with that of the initial active substance. Let C represent an asymmetric carbon



(I.) (II.)

atom, and A, B, D, and E the atoms or radicals linked to it. C, D, and E are supposed to lie in the plane of the paper, with A above and B below this plane. If now the atom E is split off, the configuration (I) is formed, and the remaining radicals are assumed to oscillate as the result of this disturbance. For simplicity, I shall consider the oscillation of only one radical, say D, between the

positions occupied in (I) *and* (II). *Whether inversion takes place or not will now depend upon whether the atom, ion, or radical* X *which enters the molecule instead of* E *is able to do so while* D *is* still upon its original side of the plane ACB, as in (I), or has passed it, as in (II). (The above representation is purely diagrammatic and makes no assumption as to the actual distribution of the four directed valency sources, but merely postulates a disturbance among them when one is temporarily out of action.)

From these conceptions we can derive a quantitative theory of the Walden inversion based upon the time of oscillation θ of the molecule, the concentrations, and the activity conditions in the solution. Of these factors, at present we know nothing of the time of oscillation and very little about the activity coefficients in such high concentrations as are usually employed in researches on the subject. Moreover, most of the experiments bearing on this inversion were carried out under conditions in which temperature and concentration were varied during the experiment in such a way as to preclude any calculation of the result, but Holmberg's experiments upon the reaction between xanthogenates and active halogenosuccinic acids (*loc. cit.*) are so precise that it is possible to apply to them the equation deduced below.

We assume that the fraction n of the reaction product which retains its original configuration is proportional to the probability that the oscillating molecule reacts with the entering ion X while still in configuration (I); this probability will evidently increase with the length of the time of oscillation and with the speed of the reaction between the single oscillating molecule and X.

Introducing the kinetic activity factor of Brönsted (*Z. physikal. Chem.*, 1922, **102**, 169) in the expression for the reaction velocity, we get the equation $n = kc_X f_1 f_2 \theta / f_{1,2}$ where c_X denotes the mean concentration of X at the beginning and end of the reaction, and f_1, f_2, and $f_{1,2}$ respectively denote the activity coefficients of the oscillating molecule, of X, and of the compound resulting from the union of these two. We can obtain the same equation from Brönsted's formula for the velocity of a bimolecular reaction, *viz.*, $-dc_1/dt = k'c_1c_2f_1f_2/f_{1,2}$; for if we replace dt by $\theta/4$ and let subscripts 1 and X refer to the oscillating molecule and to X respectively, we have

$$n = dc_1/c_1 = k'c_X(f_1f_X/f_{1,X})(\theta/4) \quad . \quad . \quad . \quad . \quad (a)$$

If, moreover, for lack of knowledge, we assume that θ depends only upon the nature of the oscillating molecule and is independent of the potential in the solution, θ can be included in the constant and the equation takes the form

$$n = kc_X f_1 f_X / f_{1,X} \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

We shall now test the application of equation (*b*) to Holmberg's experiments, but quantitative agreement with his results cannot be expected, owing to the nature of our approximations and to our lack of precise data relating to activity coefficients.

The first reaction to be considered is that between potassium, sodium, calcium, barium, and strontium salts of *l*-bromosuccinic acid and alkali xanthogenates $\bar{O}\cdot CO\cdot CH_2\cdot CHBr\cdot CO\cdot \bar{O} + CS(OEt)\cdot \bar{S} \longrightarrow \bar{O}\cdot CO\cdot CH_2\cdot CH[S\cdot CS(OEt)]\cdot CO\cdot \bar{O} + \bar{Br}$, which is assumed to take place in two steps, *viz.*, (1) a spontaneous splitting off of the bromine atom : $\bar{O}\cdot CO\cdot CH_2\cdot CHBr\cdot CO\cdot \bar{O} \longrightarrow \bar{O}\cdot CO\cdot CH_2\cdot \overset{+}{C}H\cdot CO\cdot \bar{O} + \bar{Br}$, and (2) an addition of the xanthogenate ion (denoted by X) :

$$\bar{O}\cdot CO\cdot CH_2\cdot \overset{+}{C}H\cdot CO\cdot \bar{O} + \bar{X} \longrightarrow \bar{O}\cdot CO\cdot CH_2\cdot CHX\cdot CO\cdot \bar{O}$$

The activity coefficient f_1 for the amphoteric ion $\bar{O}\cdot CO\cdot CH_2\cdot \overset{+}{C}H\cdot CO\cdot \bar{O}$, with an excess of one negative electric charge, is assumed to be approximately equal to that of an ordinary univalent ion; and for both f_1 and f_X we shall use the values of a commoner uni-univalent salt, silver nitrate being chosen for this purpose since its values are known for high ionic strengths (Lewis and Randall, "Thermodynamics," p. 363), and its structure is not so simple as that of the alkali chlorides, which are therefore less comparable with the larger ions involved here.

For the activity coefficient $f_{1,X}$ *of the bivalent ion*

$$\bar{O}\cdot CO\cdot CH_2\cdot CHX\cdot CO\cdot \bar{O},$$

I have chosen the values for magnesium sulphate in pure solutions of the same ionic strength (see Rørdam, "Studies on Activity," Copenhagen, 1925) up to 0·5*M*-solutions, and values for higher concentrations have been calculated from the freezing-point data of Loomis (Landolt–Börnstein, "Tabellen," 5th edition, 3070) by use of the equation $\log f = -0{\cdot}4343\left[(1-\phi) + \int_0^c \frac{1-\phi}{c}dc\right]$, f being the activity coefficient, c the concentration, and $\phi = i/2$ (i = van 't Hoff's factor). The data thus used are collected in Table I, *where the ionic strength* μ *is added. The assumption* that the activity coefficient of a given electrolyte is the same in all

TABLE I.

$MgSO_4$ (mol./l.).	f.	μ.	$MgSO_4$ (mol./l.).	f.	μ.
0·1	0·212	0·4	1·2	0·077	4·8
0·2	0·152	0·8	1·4	0·073	5·6
0·4	0·114	1·6	1·6	0·071	6·4
0·6	0·102	2·4	1·8	0·071	7·2
0·8	0·092	3·2	2·0	0·073	8·0
1·0	0·084	4·0			

›lutions of the same ionic strength (Lewis and Randall, *J. Amer. hem. Soc.*, 1921, **43**, 1112) is well known to be strictly valid only dilute solutions, but of necessity we apply it here up to greater oncentrations.

In Table II all Holmberg's data relevant to these experiments ·e collected. For the calculation of n from equation (*b*), the npirical value $k = 200$ has been employed. (For experiments here the ionic strength exceeds 6, no calculations have been made, ie basis for the calculation of the activity coefficients here seeming

TABLE II.

(Bs = Bromosuccinate radical; X = Xanthogenate radical.)

o.	Composition of mixture.	% *d*-Acid, found.	μ.	$f_1 = f_X$.	$f_{1,X}$.	*n*, calc.
	0·51 Na_2Bs; 0·61 NaX	35·5	2·14	0·273	0·103	51
	,, ,, ,, ,, ; 5·0 NaBr	44·2	7·14	0·080	0·072	—
	0·12 ,, 0·14 ,,	20·1	0·50	0·526	0·190	23
	0·8 ,, 0·75 KX	46·5	3·15	0·202	0·090	34
	0·5 ,, 1·1 ,,	67·1	2·60	0·245	0·100	106
	0·75 K_2Bs; 0·96 ,, ; 1·6 KBr	49·2	4·80	0·150	0·077	35
	,, ,, ,, ,, ; 4·0 ,,	50·0	7·21	0·080	0·072	—
	0·11 ,, 0·18 ,,	30·3	0·51	0·526	0·190	38
	0·08 CaBs; 0·10 NaX	20·1	0·42	0·552	0·205	19
	0·4 ,, 0·5 KX	48·4	2·10	0·273	0·103	42
	0·08 ,, 0·10 ,,	22·8	0·42	0·552	0·205	19
	0·8 BaBs; 1·0 ,,	53·8	4·20	0·175	0·080	46
	,, ,, ,, ,, ; 0·8 $BaBr_2$	63·8	6·60	0·100	0·071	—
	0·10 ,, 0·12 ,,	23·3	0·52	0·526	0·190	21
	0·8 SrBs; 1·0 ,,	59·3	4·20	0·175	0·080	46
	,, ,, ,, ,, ; 0·8 $SrBr_2$	69·4	6·60	0·100	0·071	—
	,, ,, 1·7 ,,	81·7	4·90	0·145	0·077	71
	0·10 ,, 0·12 ,,	20·1	0·52	0·526	0·190	21
	0·27 ,, 0·29 ,,	44·2	1·37	0·340	0·120	31
	,, ,, 0·87 ,,	70·4	1·95	0·280	0·105	110

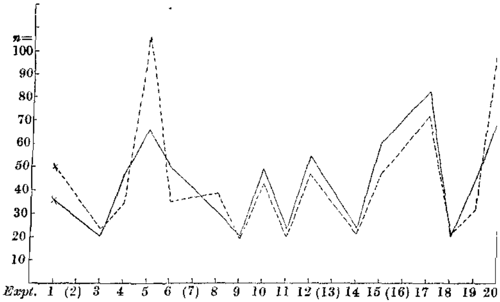
›o uncertain.) The third column of the table contains the per·ntage of dextrorotatory xanthogeno-succinic acid found by olmberg in the partly active acid resulting from the experiments. the theory now *propounded is valid*, it affords a means whereby decide which of the two possible optical isomerides that may be rmed possesses the same steric configuration as the initial active mponent in a reaction leading to a Walden inversion. Hence may conclude from the calculations that *d*-xanthogenosuccinic *id and l*-bromosuccinic acid have corresponding configurations.

The results *shown* in Table II are represented graphically in g. 1, the calculated (broken line) and experimental (full line) dues of n being given in connexion with the series number of e experiment. These curves show that variation in experimental dues is closely related to that in the calculated values. In view the *fact that the individual peculiarities of the activity coefficients*

and the deviations in the "rule of ionic strength" are both ver marked at the high concentrations used, the agreement seem fairly good.

In spite of the accuracy of Holmberg's experiments, it is possib that the percentages found by him do not agree exactly with th total amount formed in the reaction, for the product was obtaine by spontaneous crystallisation from the more or less concentrate salt solutions, and in most cases the solubilities of racemic an corresponding active substances are different in, and perhaps als unequally influenced by, different salt concentrations.

FIG. 1.

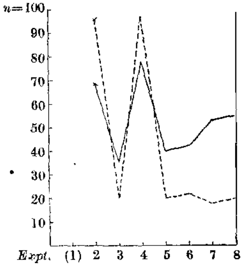


In future experimental researches in this field, it would be of interest to avoid uncertainty of this sort by determining the composition optically, without isolation of the reaction product; and in order to test the validity of the present theory it will be necessary to use reaction conditions such that the activity coefficients can be accurately calculated. The theory suggests possibilities for planning experiments which may throw more light upon the Walden inversion. If valid, it will account for the influence of the concentrations of reagents and of salts present in the solution, as well as of the nature of the solvent.

The literature affords only one other series of experiments suitable for testing the present theory, *viz.*, those of Holmberg (*Arkiv. Kemi, Min. Geol.*, 1915, **6**, 1) on the reaction between hydrosulphides and salts of *l*-bromosuccinic acid, which is assumed to occur in two stages exactly like the foregoing reaction. As the SH′ ion is considerably less complicated in structure than the

xanthogenate ion, its activity coefficient is more appropriately represented by that of sodium nitrate than that of silver nitrate; the necessary values are only available up to 0·5*M* (Rørdam, *op. cit.*), and values for higher concentrations are therefore obtained by plotting these values by the side of those already used for silver nitrate and extrapolating the curve so that it remains parallel to the curve for silver nitrate.

FIG. 2.



The value used for k is 200 as before. The agreement between calculated and observed values is not so good in this case, perhaps owing to the less definite composition of hydrosulphide solutions and to their instability. The data appear in Table III and are represented in Fig. 2 as for the former reaction. The displacement of the curve when foreign salts are present cannot yet be explained.

TABLE III.

No.	Composition of mixture.	% d-Acid found.	μ.	$f_1 = f_{SH}$.	$f_{1,SH}$.	n, calc.
1.	1·0 K_2Bs; 1·0 KSH	95·9	4·0	0·33	0·084	—
2.	0·5 ,, 0·5 ,,	68·6	2·0	0·45	0·105	96
3.	0·1 ,, 0·1 ,,	35·2	0·4	0·65	0·212	20
4.	0·1 ,, 0·3 ,,	77·7	0·6	0·59	0·180	97
5.	,, ,, 0·1 ,, ; 0·5 K_2SO_4	40·3	1·9	0·46	0·107	20
6.	,, ,, ,, ,, ; 1·0 KBr	42·5	1·4	0·50	0·115	22
7.	,, ,, ,, ,, ; 2·0 KBr	53·2	2·4	0·43	0·102	18
8.	,, ,, ,, ,, ; 0·5 $SrBr_2$	55·4	1·9	0·46	0·107	20

Finally, it may be remarked that a complete theoretical calculation should perhaps take into consideration the possibility that some of the oscillating molecules ean escape reaction both while in configuration (I) and in configuration (II) for the first time, and only react during a subsequent oscillation. It is also possible that very accurate experiments would show that the time of oscillation of the molecule is influenced by the potential in the solution. The conception of the Walden inversion now put forward seems to have the advantage that it is capable of experimental verification.

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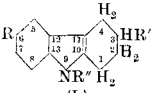
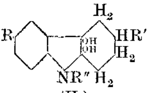
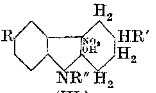
CCCXXV.—*Derivatives of Tetrahydrocarbazole. Part VII. Reactions of 3-Methyltetrahydrocarbazole, 6-Chlorotetrahydrocarbazole, and their Acyl Derivatives.*

By Sydney Glenn Preston Plant and Reginald John Rosser.

Some of the most interesting reactions observed with tetrahydrocarbazole (I; R = R′ = R″ = H) are those of its 9-acyl derivatives with nitric acid (Perkin and Plant, J., 1923, **123**, 676). Besides simple nitro-derivatives in all cases, the 9-benzoyl compound forms a product by the addition of OH and NO_2 to the double linkage, and the 9-acetyl, 9-carbethoxy-, and 9-phenylacetyl derivatives add two hydroxyl radicals to this linkage. The reason for this remarkable difference between 9-benzoyltetrahydrocarbazole and the other 9-acyl derivatives investigated has never been explained, although, of course, it may be quite fortuitous. The present work was therefore undertaken with the view of determining (1) how far these additive reactions can be carried out with other tetrahydrocarbazole compounds, and (2) the effect of the nature and position of substituents upon the reactions. The observations of Manjunath and Plant (J., 1926, 2260) with 9-acetyl-6-methyltetrahydrocarbazole indicated that *3-methyltetrahydrocarbazole* (I; R = R″ = H; R′ = Me), in which the methyl group is in the reduced part of the molecule, and 6-chlorotetrahydrocarbazole (I; R′ = R″ = H; R = Cl), containing a negative atom, would be suitable for investigation. The former has been obtained by Fischer's indole synthesis from


(I.)


(II.)


(III.)

4-methylcyclohexanone phenylhydrazone, and, on nitration in concentrated sulphuric acid solution, it yielded a single product, which was shown to be *6-nitro-3-methyltetrahydrocarbazole* (I; R = NO_2; R′ = Me; R″ = H). In order to identify some of the derivatives obtained in this work, 6-nitro-3-methyltetrahydrocarbazole and *8-nitro-3-methyltetrahydrocarbazole* have been synthesised by eliminating ammonia from *4-methylcyclohexanone* p- and o-*nitrophenylhydrazones*, respectively. The isomeric 5(or 7)-*nitro-* and 7(or 5)-*nitro-3-methyltetrahydrocarbazoles* were both obtained from *4-methylcyclohexanone* m-*nitrophenylhydrazone*. It is not possible to say which of these is really the 5- and which the 7-nitro-derivative, whilst

it is interesting to note that *cyclo*hexanone *m*-nitrophenylhydrazone yields only one compound, assumed to be 7-nitrotetrahydrocarbazole (Borsche, Witte, and Bothe, *Annalen*, 1908, **359**, 53), under similar conditions. 3-Methyltetrahydrocarbazole has been converted into its 9-*acetyl* derivative with acetic anhydride, but the corresponding 9-*benzoyl* and 9-*carbethoxy*-compounds were made by first obtaining *magnesium* 9-3-*methyltetrahydrocarbazyl iodide* (I; R = H; R′ = Me; R″ = MgI) and subsequently treating this with benzoyl chloride and ethyl chloroformate, respectively. When 9-acetyl-3-methyltetrahydrocarbazole was treated with nitric acid in acetic acid solution, 5(or 7)-*nitro-9-acetyl-3-methyltetrahydrocarbazole* and 10 : 11-*dihydroxy-9-acetyl-3-methylhexahydrocarbazole* (II; R = H; R′ = Me; R″ = Ac) were obtained, but the exact nature of the product depended on the conditions used (p. 2458). The position of the nitro-group in the former of these two derivatives was established by hydrolysis to one of the isomeric nitro-compounds obtained synthetically from 4-methyl*cyclo*hexanone *m*-nitrophenylhydrazone. In view of the results obtained with tetrahydrocarbazole itself and the assumptions then made (Perkin and Plant, J., 1921, **119**, 1825), it seems advisable to avoid confusion by regarding this nitro-compound as the 5-nitro-derivative, but to admit the possibility of an alternative structure by adopting the designation "5(or 7)-nitro." The dihydroxy-compound obtained in this reaction was found to lose water on boiling with acetic anhydride, presumably to give 6-*acetyl-3-methyl-ψ-indoxyl*spiro*cyclopentane*, by a reaction analogous to that observed with the parent substance (Perkin and Plant, *loc. cit.*). 9-Benzoyl-3-methyltetrahydrocarbazole, on treatment with nitric acid in acetic acid solution, yielded a mixture of 11-*nitro-10-hydroxy-9-benzoyl-3-methylhexahydrocarbazole* (III; R = H; R′ = Me; R″ = Bz) and 5(or 7)-*nitro-9-benzoyl-3-methyltetrahydrocarbazole*, whilst under similar conditions ethyl 3-methyltetrahydrocarbazole-9-carboxylate behaved like the 9-acetyl derivative and gave a mixture of *ethyl* 5(or 7)-*nitro-3-methyltetrahydrocarbazole-9-carboxylate* and *ethyl* 10 : 11-*dihydroxy-3-methylhexahydrocarbazole-9-carboxylate* (II; R = H; R′ = Me; R″ = CO_2Et). It is apparent, therefore, that in general the results obtained with 3-methyltetrahydrocarbazole are similar to those in the case of tetrahydrocarbazole itself, but the addition products were not produced quite so readily and were more difficult to isolate.

The three isomeric mononitro-derivatives of 6-chlorotetrahydrocarbazole were obtained synthetically, the 8-*nitro*-compound from cyclo*hexanone 4-chloro-2-nitrophenylhydrazone*, and a mixture of the 5(or 7)- and 7(or 5)-*nitro*-compounds from cyclo*hexanone 4-chloro-3-nitrophenylhydrazone*. When 6-chlorotetrahydrocarbazole was

nitrated directly in sulphuric acid, 5(or 7)-nitro-6-chlorotetrahydrocarbazole was produced. *6-Chloro-9-acetyltetrahydrocarbazole* was prepared from its parent substance by direct acetylation, but the *9-benzoyl* and *9-carbethoxy*-derivatives were obtained by employing Grignard reactions as in the case of the corresponding products from 3-methyltetrahydrocarbazole. When nitric acid acted on this 9-acetyl compound in acetic acid solution, both *6-chloro-5(or 7)-nitro-9-acetyltetrahydrocarbazole* and *6-chloro-10 : 11-dihydroxy-9-acetylhexahydrocarbazole* (II; R = Cl; R′ = H; R″ = Ac) were produced, but the relative amounts could be varied by altering the conditions. From 6-chloro-9-benzoyltetrahydrocarbazole both *6-chloro-5(or 7)-nitro-9-benzoyltetrahydrocarbazole* and *6-chloro-11-nitro-10-hydroxy-9-benzoylhexahydrocarbazole* (III; R = Cl; R′ = H; R″ = Bz) were obtained, but in the case of ethyl 6-chlorotetrahydrocarbazole-9-carboxylate unexpected results were observed. *Ethyl 6-chloro-5(or 7)-nitrotetrahydrocarbazole-9-carboxylate* was isolated, but the second product proved to be *ethyl 6-chloro-11-nitro-10-hydroxyhexahydrocarbazole-9-carboxylate* (III; R = Cl; R′ = H; R″ = CO_2Et), thus providing an example of the addition of OH and NO_2 to the double linkage in a 9-carbethoxy-derivative. When a solution of this addition compound in alcohol was boiled, a product, which appeared on analysis to be *ethyl 6-chloro-10 : 11-dihydroxyhexahydrocarbazole-9-carboxylate* (II; R = Cl; R′ = H; R″ = CO_2Et), was obtained, apparently by the replacement of NO_2 by OH. The products resulting from the addition of nitric acid decompose, on melting, with the evolution of oxides of nitrogen. The preparation of these compounds from 6-chlorotetrahydrocarbazole required more vigorous conditions than in the case of tetrahydrocarbazole itself.

Since hexahydrocarbazole has been shown to exist in two stereoisomeric modifications (Gurney, Perkin, and Plant, J., 1927, 2676), it follows that theoretically four modifications of 3-methylhexahydrocarbazole might appear during the reduction of 3-methyltetrahydrocarbazole. Two of these would result from the *cis*-addition of hydrogen at the double linkage and would be less strained than the other two, which would result from the *trans*-addition of hydrogen. From the results obtained in the reduction of tetrahydrocarbazole, it might be expected that the former two would be formed in relatively great amounts, but that only very small quantities of the latter two would be present in the reduction product. This point has been investigated, but only one product (presumably one of the *cis*-modifications) resulted on electrolytic reduction. This, which melts at 58·5°, has been called *3-methylhexahydrocarbazole* (A). When, however, 3-methyltetrahydrocarbazole was reduced with tin

and hydrochloric acid in aqueous alcohol, a small quantity of a second form, *3-methylhexahydrocarbazole* (B), m. p. 128°, was isolated in addition to the modification (A), which formed the main product. It is hardly possible, on account of the small yield of 3-methylhexahydrocarbazole (B), to say whether this is the second *cis*-modification or one of the two *trans*-forms. It is theoretically possible for all the products formed by addition of OH and NO_2, or OH and OH, at the double linkage in tetrahydrocarbazole to exist in more than one stereoisomeric modification, but so far in no case has more than a single form been isolated.

EXPERIMENTAL.

3-Methyltetrahydrocarbazole and its Nitro-derivatives.—The crude, solid *4-methyl*cyclo*hexanone phenylhydrazone* (7 g.), obtained by mixing equal weights of 4-methyl*cyclo*hexanone and phenylhydrazine, was warmed with aqueous sulphuric acid (120 c.c. of 17%) for 15 minutes on the water-bath, with shaking. *3-Methyltetrahydrocarbazole* was isolated from alcohol in colourless, rhombic prisms, m. p. 109—110° (Found: N, 7·5. $C_{13}H_{15}N$ requires N, 7·6%).

From a solution of *p*-nitrophenylhydrazine (1·7 g.) and 4-methyl*cyclo*hexanone (1·2 g.) in hot alcohol, *4-methyl*cyclo*hexanone* p-*nitrophenylhydrazone* separated, on cooling, in yellow needles, m. p. 128·5°, and, after treatment with boiling 25% sulphuric acid for a few minutes, it yielded *6-nitro-3-methyltetrahydrocarbazole*, which crystallised from alcohol (charcoal) in brown prisms, m. p. 165—166° (Found: N, 12·2. $C_{13}H_{14}O_2N_2$ requires N, 12·2%). By a similar process, *4-methyl*cyclo*hexanone* o-*nitrophenylhydrazone* was obtained in crimson prisms, m. p. 59°, and converted into *8-nitro-3-methyltetrahydrocarbazole*, which separated from alcohol in bright red needles, m. p. 188° (Found: N, 12·1%). *4-Methyl*cyclo*hexanone* m-*nitrophenylhydrazone*, from alcohol in orange-red prisms, m. p. 80—81°, yielded a mixture with boiling 27% sulphuric acid. The filtered solution of the crude product (6 g.) in hot alcohol deposited, on cooling and leaving for 24 hours, *5(or 7)-nitro-3-methyltetrahydrocarbazole* in yellow needles, m. p. 188° (Found: N, 12·0%), whilst, on concentration of the mother-liquor, a further quantity, contaminated with a little of the isomeride, was obtained. The crude *7(or 5)-nitro-3-methyltetrahydrocarbazole* was then isolated by adding water to the mother-liquor, and purified by crystallisation from chloroform, separating in orange-red plates, m. p. 175° (Found: N, 12·2%). These two nitro-compounds were formed in approximately equal amounts.

A solution of 3-methyltetrahydrocarbazole (10·6 g.) in concentrated sulphuric acid (70 c.c.) was kept at − 10° and treated grad-

ually with pulverised potassium nitrate (5·9 g.), with continuous stirring. After being poured on ice and collected as quickly as possible, the product, when dried in a desiccator, melted at 159°. It separated from alcohol in brown prisms, m. p. 165—166°, and was shown to be 6-nitro-3-methyltetrahydrocarbazole by a mixed m. p. determination. No other substance could be isolated from the reaction mixture.

Action of Nitric Acid on 9-Acetyl-3-methyltetrahydrocarbazole.— When a solution of 3-methyltetrahydrocarbazole in 2½ times its weight of acetic anhydride was boiled under reflux for 3 hours and cooled, *9-acetyl-3-methyltetrahydrocarbazole* separated, and was obtained from glacial acetic acid in colourless needles, m. p. 108·5° (Found : N, 6·1. $C_{15}H_{17}ON$ requires N, 6·2%). When a solution of the acetyl derivative (3·6 g.) in glacial acetic acid (50 c.c.) was treated with nitric acid (1·8 g., *d* 1·42, dissolved in a little acetic acid) at room temperature, *5(or 7)-nitro-9-acetyl-3-methyltetrahydrocarbazole* separated during 24 hours in clusters of yellow needles, m. p. 134° (after recrystallisation from alcohol) (Found : N, 10·3. $C_{15}H_{16}O_3N_2$ requires N, 10·3%). A mixture of this nitro-compound (1·5 g.), sodium hydroxide (9 g.), alcohol (60 c.c.), and water (60 c.c.) was boiled for some time and then diluted with water. When the product was crystallised from alcohol, 5(or 7)-nitro-3-methyltetrahydrocarbazole separated in orange prisms, m. p. 187°. It was shown by a mixed m. p. determination to be identical with one of the products obtained from 4-methyl*cyclo*hexanone *m*-nitrophenylhydrazone. The m. p. of the mixture with 8-nitro-3-methyltetrahydrocarbazole was much lower.

When 9-acetyl-3-methyltetrahydrocarbazole (18 g.) in acetic acid (66 c.c.) was treated at 50° with nitric acid (9·2 g. ; *d* 1·42) in acetic acid (10 c.c.), 5(or 7)-nitro-9-acetyl-3-methyltetrahydrocarbazole (3 g.) again separated over-night, but after pouring the mother-liquor into water, adding aqueous sodium hydroxide until nearly neutral, and stirring, a product was obtained which could be easily collected and after being dried in a desiccator yielded *10 : 11-dihydroxy-9-acetyl-3-methylhexahydrocarbazole* on crystallisation from benzene. After recrystallisation from alcohol, it was obtained in almost colourless plates, m. p. 189—190° (Found : N, 5·4. $C_{15}H_{19}O_3N$ requires N, 5·4%). When a solution of this dihydroxy-compound (2·5 g.) in acetic anhydride (40 c.c.) was boiled under reflux for 2 hours, cooled, and shaken with water, the product, after crystallisation from alcohol, yielded *6-acetyl-3-methyl-ψ-indoxyl*spiro*cyclopentane* in colourless plates, m. p. 93·5° (Found : N, 5·8. $C_{15}H_{17}O_2N$ requires N, 5·8%). *3-Methyl-ψ-indoxyl*spiro*cyclopentane*, obtained from its acetyl derivative by hot aqueous-alcoholic

potassium hydroxide and subsequent addition of water, separated from alcohol in colourless prisms, m. p. 114·5°.

Action of Nitric Acid on 9-Benzoyl-3-methyltetrahydrocarbazole.—3-Methyltetrahydrocarbazole (14·7 g.) was added in portions to a solution of magnesium (1·9 g.) in ethyl iodide (12·8 g.) and dry ether (180 c.c.), and, after the evolution of ethane had ceased, benzoyl chloride (11·4 g.) was gradually introduced with shaking. After some time, ice and dilute hydrochloric acid were added, the ethereal solution was dried with calcium chloride, the ether removed, and the residual red oil distilled under reduced pressure. The distillate, collected at 255—265°/11 mm., was crystallised from alcohol, from which *9-benzoyl-3-methyltetrahydrocarbazole* separated in colourless prisms, m. p. 99° (Found: N, 4·9. $C_{20}H_{19}ON$ requires N, 4·8%).

When a solution of 9-benzoyl-3-methyltetrahydrocarbazole (2·6 g.) in glacial acetic acid (47 c.c.) was treated with nitric acid (0·9 g., *d* 1·42) at 30° and then left for 24 hours, *11-nitro-10-hydroxy-9-benzoyl-3-methylhexahydrocarbazole* separated in pale yellow prisms, m. p. 123° (decomp., with evolution of oxides of nitrogen). It separated from benzene–petroleum in small prisms, m. p. 123—124° (decomp.) (Found: N, 7·6. $C_{20}H_{20}O_4N_2$ requires N, 7·9%). When the solid precipitated by pouring the acetic acid mother-liquor into water was crystallised from methyl alcohol, *5(or 7)-nitro-9-benzoyl-3-methyltetrahydrocarbazole* separated in yellow needles, m. p. 142·5° (Found: N, 8·4. $C_{20}H_{18}O_3N_2$ requires N, 8·4%). This compound, which formed by far the greater part of the product, was hydrolysed by aqueous-alcoholic sodium hydroxide to 5(or 7)-nitro-3-methyltetrahydrocarbazole, m. p. 186°, the identity of which was established by a mixed m. p. determination with the synthetical product.

Action of Nitric Acid on Ethyl 3-Methyltetrahydrocarbazole-9-carboxylate.—*Ethyl 3-methyltetrahydrocarbazole-9-carboxylate* was prepared by the Grignard reaction, similar to that used for the 9-benzoyl derivative, ethyl chloroformate being used. It was unnecessary here to distil the crude product, and the ester separated from alcohol in colourless prisms, m. p. 66—67° (Found: N, 5·7. $C_{16}H_{19}O_2N$ requires N, 5·5%). A solution of the ester (9·2 g.) in glacial acetic acid (16 c.c.) at 25° was treated with nitric acid (3·6 g., *d* 1·42), dissolved in acetic acid (4 c.c.), the temperature not being allowed to rise above 50°. After a short time, the yellow needles, m. p. 101°, which separated, were collected and recrystallised from alcohol, from which *ethyl 5(or 7)-nitro-3-methyltetrahydrocarbazole-9-carboxylate* was isolated in yellow prisms, m. p. 104° (Found: N, 9·2. $C_{16}H_{18}O_4N_2$ requires N, 9·3%). When treated with boiling aqueous-alcoholic sodium hydroxide, this product yielded 5(or 7)-nitro-3-methyltetrahydrocarbazole, m. p. 187° (mixed m. p. 187°). The

acetic acid mother-liquor deposited, on being kept for 24 hour further quantity, m. p. 100°, of this nitro-derivative. When filtrate was subsequently concentrated by keeping in a vacu desiccator over solid sodium hydroxide for several days a sec product, m. p. 121—129°, separated, and, after recrystallising from alcohol, *ethyl* 10 : 11-*dihydroxy-3-methylhexahydrocarbazol carboxylate* was obtained in clusters of small, colourless pris m. p. 135° (Found : N, 4·7. $C_{16}H_{21}O_4N$ requires N, 4·8%).

Reduction of 3-Methyltetrahydrocarbazole.—A mixture of 3-meth tetrahydrocarbazole (10 g.), alcohol (20 c.c.), concentrated hyd chloric acid (20 c.c.), and granulated tin (20 g.) was boiled un reflux for 5 hours, filtered, as much alcohol as possible was distil off, and the residue was made alkaline with sodium hydroxide (2(in concentrated aqueous solution). The solid product was collec on asbestos and extracted with ether, the filtrate being also extrac with ether. The solid then remaining was ground with aque sodium hydroxide and again extracted with ether. The uni ethereal solutions were dried with potassium carbonate, and the c residue remaining after removal of the solvent was crystallised fr alcohol, 3-*methylhexahydrocarbazole* (A) separating in colourl prisms, m. p. 58·5° (Found : C, 83·6; H, 9·1; N, 7·4. $C_{13}H_1$ requires C, 83·4; H, 9·1; N, 7·5%). On concentrating the alcoho mother-liquor, further quantities of 3-methylhexahydrocarbazole (were obtained, but ultimately a product, melting at 50—90°, beg to separate. At this point the whole was dissolved in 60% sulphu acid and then diluted with water to precipitate the very sm quantity of non-basic, unreduced 3-methyltetrahydrocarbaz which was present. After filtration and basification by addition concentrated aqueous ammonia, the resulting solid was recrystallis from alcohol, and 3-*methylhexahydrocarbazole* (B) separated in colou less needles, m. p. 128° (Found : C, 83·8; H, 9·4. $C_{13}H_{17}N$ requir C, 83·4; H, 9·1%).

A solution of 3-methyltetrahydrocarbazole (10 g.) in 60% sulphur acid (250 c.c.) was submitted to electrolytic reduction in the catho compartment of an electrolytic cell, lead electrodes and a curre of 5·5 amps. (0·03 amp. per sq. cm. of cathode) for 16 hours at roo temperature being used, but, on dilution with water, unchang 3-methyltetrahydrocarbazole was recovered. The reduction w subsequently repeated, the cell being immersed in boiling water; th solution was then diluted with its own volume of water, filtere and made alkaline with ammonia. The product was taken up i ether, and, after crystallisation from petroleum, 3-methylhexahydr carbazole (A) was obtained in colourless plates, m. p. 57—58°, it identity with the substance previously described being establishe

by a mixed m. p. determination. The presence of a second stereoisomeride in this product was not observed.

When 3-methylhexahydrocarbazole (A) was shaken with an equal weight of benzoyl chloride in the presence of dilute aqueous sodium hydroxide, and the product was crystallised from alcohol, 9-*benzoyl*-3-*methylhexahydrocarbazole* (A) was obtained in colourless needles, m. p. 81·5° (Found : N, 4·8. $C_{20}H_{21}ON$ requires N, 4·8%). 9-*Acetyl*-3-*methylhexahydrocarbazole* (A) was isolated by boiling a solution of the base in acetic anhydride for 20 minutes and subsequently shaking with dilute aqueous sodium carbonate, and was obtained from alcohol in colourless, rhombic prisms, m. p. 101°. The *picrate* of 3-methylhexahydrocarbazole (A) separated from toluene in yellow prisms, m. p. 115—116°.

Nitro-derivatives of 6-*Chlorotetrahydrocarbazole*.—6-Chlorotetrahydrocarbazole, prepared as described by Borsche, Witte, and Bothe (*loc. cit.*), was obtained from alcohol in colourless prisms, m. p. 144°. A solution of this chloro-compound (2 g.) in concentrated sulphuric acid (13 c.c.) was treated gradually at − 10° with powdered potassium nitrate (1·15 g.), with continuous stirring, and the whole was then poured on ice. When the product was crystallised from alcohol and then ethyl acetate, 6-*chloro*-5(or 7)-*nitrotetrahydrocarbazole* separated in yellow plates, m. p. 183·5° (Found : N, 11·2. $C_{12}H_{11}O_2N_2Cl$ requires N, 11·2%). A mixed m. p. determination showed this product to be identical with the 6-chloro-5(or 7)-nitrotetrahydrocarbazole described below.

4-Chloro-3-nitroaniline (12·5 g.) was dissolved in a warm mixture of concentrated hydrochloric acid (21 c.c.) and water (20 c.c.), the whole was rapidly cooled in a freezing mixture, and diazotised with aqueous sodium nitrite (6 g.). The filtered liquid was then added gradually during 10 minutes to a well-cooled mixture of saturated aqueous ammonium sulphite (40 c.c.) and concentrated ammonia (8 c.c.), and, after ½ hour, concentrated hydrochloric acid (70 c.c.) was added, the mixture warmed to 30°, and left over-night. The solid product was heated at 80° for a short time with concentrated hydrochloric acid (20 c.c.), and, after cooling and standing, the hydrazine hydrochloride was collected, dissolved in boiling water (200 c.c.), and the filtered solution treated with sodium acetate. After crystallisation from methyl alcohol, 4-*chloro*-3-*nitrophenylhydrazine* separated in orange needles, m. p. 109° (Found : N, 22·1. $C_6H_6O_2N_3Cl$ requires N, 22·4%). cyclo*Hexanone* 4-*chloro*-3-*nitrophenylhydrazone* separated from a hot alcoholic solution of 4-chloro-3-nitrophenylhydrazine (2·5 g.) and *cyclo*hexanone, (1·5 g.), on cooling, in red prisms, m. p. 106—107° (Found: N, 15·7. $C_{12}H_{14}O_2N_3Cl$ requires N, 15·7%). When the mixture obtained by

treating this hydrazone (7·5 g.) with boiling aqueous sulphuric acid (170 c.c. of 25%) for 10 minutes was crystallised from methyl alcohol, 6-chloro-5(or 7)-nitrotetrahydrocarbazole separated in brown needles, m. p. 184°, and was found to be identical with the product of the direct nitration of 6-chlorotetrahydrocarbazole. After collecting a further quantity of the same derivative by concentrating the methyl-alcoholic mother-liquor, the remaining filtrate was evaporated to dryness and the residue crystallised from benzene. 6-*Chloro-7*(or 5)-*nitrotetrahydrocarbazole* then separated in orange needles, m. p. 162° (Found: N, 11·1. $C_{12}H_{11}O_2N_2Cl$ requires N, 11·2%). These two isomeric nitro-compounds appeared to be produced in approximately equal amounts.

By a process essentially similar to that described above, 4-chloro-2-nitroaniline was converted into 4-*chloro-2-nitrophenylhydrazine*, which was isolated from alcohol in red needles, m. p. 134° (Found: N, 22·0%). cyclo*Hexanone 4-chloro-2-nitrophenylhydrazone*, which separated from alcohol in red needles, m. p. 101°, was converted into 6-*chloro-8-nitrotetrahydrocarbazole* by treating it for 20 minutes with boiling 30% sulphuric acid, the product being obtained from alcohol (charcoal) in orange-red needles, m. p. 213° (Found: N, 11·3%).

Action of Nitric Acid on 6-Chloro-9-acetyltetrahydrocarbazole.—The acetylation of 6-chlorotetrahydrocarbazole proved to be a slow reaction, but when a solution of the substance in four times its weight of acetic anhydride containing 2 drops of concentrated sulphuric acid was boiled for 24 hours, 6-*chloro-9-acetyltetrahydrocarbazole* separated, on cooling, in colourless needles, m. p. 136° (unaltered by recrystallisation from acetic acid) (Found: N, 5·4. $C_{14}H_{14}ONCl$ requires N, 5·6%). Nitric acid (*d* 1·42) did not react with this acetyl derivative in acetic acid until the temperature reached about 80°. A solution of the compound (8·8 g.) in glacial acetic acid (48 c.c.) at 90° was treated with nitric acid (3·5 g., *d* 1·42), in a little acetic acid. A vigorous reaction took place and the solution boiled. During 16 hours a yellow product, m. p. 206—207°, separated, and, on recrystallising this from acetic acid, 6-*chloro-10 : 11-dihydroxy-9-acetylhexahydrocarbazole* was obtained in colourless prisms, m. p. 222° (Found: N, 4·9. $C_{14}H_{16}O_3NCl$ requires N, 5·0%). If the temperature during this reaction was maintained at 80°, the product, which separated on standing for 24 hours, was clearly a mixture of colourless prisms and yellow needles. After several crystallisations from alcohol, a small quantity of 6-*chloro-5*(or 7)-*nitro-9-acetyltetrahydrocarbazole* was isolated in yellow needles, m. p. 184·5—185·5° (Found: N, 9·6. $C_{14}H_{13}O_3N_2Cl$ requires N, 9·6%). This product was much more readily obtained by treating the 9-acetyl compound (0·8 g.) in acetic acid (15 c.c.) at 55° with

fuming nitric acid (0·25 g., *d* 1·5), whereupon it crystallised on standing. On hydrolysis, by boiling its solution in aqueous-alcoholic sodium hydroxide, it yielded 6-chloro-5(or 7)-nitrotetrahydrocarbazole, m. p. 184°, identical with one of the products from *cyclo*hexanone 4-chloro-3-nitrophenylhydrazone.

Action of Nitric Acid on 6-Chloro-9-benzoyltetrahydrocarbazole.—The benzoylation of 6-chlorotetrahydrocarbazole was accomplished as described for the 3-methyl derivative, but it was unnecessary to distil the crude product. After crystallisation from alcohol, *6-chloro-9-benzoyltetrahydrocarbazole* was obtained in colourless needles, m. p. 122—123° (Found: N, 4·4. $C_{19}H_{16}ONCl$ requires N, 4·5%). When a solution of this benzoyl compound (4·1 g.) in glacial acetic acid (20 c.c.) at 80° was treated with nitric acid (1·5 g., *d* 1·42) in a little acetic acid, yellow needles, m. p. 142°, separated gradually during 12 hours. After recrystallisation from alcohol, *6-chloro-*5(or 7)-*nitro-9-benzoyltetrahydrocarbazole* was obtained in yellow needles, m. p. 148° (Found: N, 7·8. $C_{19}H_{15}O_3N_2Cl$ requires N, 7·9%). When this product was hydrolysed by means of aqueous-alcoholic sodium hydroxide, 6-chloro-5(or 7)-nitrotetrahydrocarbazole, m. p. 184°, identical with the synthetical substance, was obtained. The acetic acid mother-liquor, on keeping, deposited first a further quantity of the nitro-compound and then a pale yellow substance, melting at 142° with evolution of oxides of nitrogen. This was clearly different from the first product, since a mixture of the two melted at 130—133°, and the evolution of oxides of nitrogen on melting is characteristic of the nitric acid addition products. The latter substance was more conveniently prepared by treating a solution of the benzoyl compound (1·8 g.) in acetic acid (10 c.c.) with fuming nitric acid (0·6 g., *d* 1·5, in a little acetic acid) at 40—50°. *6-Chloro-11-nitro-10-hydroxy-9-benzoylhexahydrocarbazole* immediately separated in colourless prisms, m. p. 147° (decomp., with evolution of oxides of nitrogen) (Found: N, 7·3. $C_{19}H_{17}O_4N_2Cl$ requires N, 7·5%).

Action of Nitric Acid on Ethyl 6-Chlorotetrahydrocarbazole-9-carboxylate.—*Ethyl* 6-*chlorotetrahydrocarbazole-9-carboxylate*, prepared by a process similar to that described for the 3-methyl derivative, separated from alcohol in colourless needles, m. p. 111—112° (Found: N, 5·1. $C_{15}H_{16}O_2NCl$ requires N, 5·0%). When the ester (2·0 g.) was treated in glacial acetic acid (6 c.c.) at 60° with nitric acid (0·7 g., *d* 1·42), the product gradually separated as a yellow solid, m. p. 120—125°. After two crystallisations from alcohol, *ethyl 6-chloro-*5(or 7)-*nitrotetrahydrocarbazole-9-carboxylate* was obtained in yellow needles, m. p. 126° (Found: N, 8·7. $C_{15}H_{15}O_4N_2Cl$ requires N, 8·7%), which, on hydrolysis with aqueous-alcoholic

sodium hydroxide, yielded 6-chloro-5(or 7)-nitrotetrahydrocarbazole, m. p. 184°, identical with the synthetical product already described. When ethyl 6-chlorotetrahydrocarbazole-9-carboxylate (2 g.) was treated in acetic acid (12 c.c.) at 40—45° with fuming nitric acid (0·55 g., *d* 1·5), a colourless product immediately separated. This melted at 136—137° with evolution of oxides of nitrogen and was clearly a nitric acid addition product. After crystallisation from ethyl acetate, *ethyl 6-chloro-11-nitro-10-hydroxyhexahydrocarbazole-9-carboxylate* was obtained in colourless prisms, m. p. 136—137° (decomp.) (Found: N, 8·1. $C_{15}H_{17}O_5N_2Cl$ requires N, 8·2%). When its solution in alcohol was boiled for an hour, the product, which separated in colourless prisms, m. p. 132°, appeared to be *ethyl 6-chloro-10 : 11-dihydroxyhexahydrocarbazole-9-carboxylate* (Found: C, 58·1; H, 5·8; N, 4·9. $C_{15}H_{18}O_4NCl$ requires C, 57·8; H, 5·8; N, 4·5%).

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CCCXXVI.—*The Decomposition of Bornyl Benzene- and Naphthalene-sulphonates by Heat. The Products of Hydrolysis of Bornyl and Menthyl Benzene- and Naphthalene-sulphonates. The Influence of Solvents on the Temperature of Decomposition of these Bornyl and Menthyl Sulphonates.*

By THOMAS STEWART PATTERSON and IRENE MARY McALPINE.

IN a recent paper (J., 1927, 349) we showed that the menthyl esters of benzene-, naphthalene-α- and naphthalene-β-sulphonic acids decomposed in two different ways according as they were (*a*) directly distilled under reduced pressure or (*b*) heated for some time before distillation. In the first case the main reaction was decomposition into menthene and the corresponding sulphonic acid, but in the second any menthene originally produced was converted into dimenthene and more complex substances.

These results seemed sufficiently interesting to make it worth while to extend the investigation to the behaviour of the corresponding bornyl esters, and for this purpose we have used mostly the *l*-bornyl derivatives, since *d*-borneol is not easily obtained in pure condition. We examined first, fairly completely, the naphthalene-β-sulphonic ester, as it is rather more easily obtained; the other esters were examined with less completeness, but sufficiently to establish similarity of behaviour in all three.

Decomposition by Distillation under Reduced Pressure.—When bornyl naphthalene-β-sulphonate was distilled from an oil-bath as rapidly as possible under a pressure of 18 mm., a small quantity (15—20% of the theoretical amount) of a clear, optically inactive liquid passed over at about 60°. This on redistillation boiled at 155—158° under ordinary pressure and solidified to a white substance, m. p. 51° (Found: C, 88·2, 88·1; H, 11·85, 11·8; *M*, cryoscopic in benzene, 137. Calc. for $C_{10}H_{16}$: C, 88·2; H, 11·8%; *M*, 136). The substance decolorised bromine and gave, when hydrogen chloride was passed through its solution in ether, a white precipitate which melted at 125—127° after recrystallisation from alcohol containing hydrogen chloride. These data indicate that the decomposition product is camphene.

The residue in the flask after the distillation of the camphene separated into two layers, the lower of which solidified. We found it best to separate these layers by dissolving the whole mass in warm water and extracting the solution with toluene. The extract was dried with calcium chloride and distilled under reduced pressure and after removal of the solvent a viscous, almost inactive liquid distilled at 168°/4 mm. (Found: C, 88·1, 88·2; H, 11·8, 11·8. Calc. for $C_{20}H_{32}$: C, 88·2; H, 11·8%). Since Tschugaev, on distilling bornyl methyl xanthogenate, obtained bornylene and a little camphene, and analogy seems to exist between the reactions of the xanthogenates and sulphonates under similar conditions (*e.g.*, menthyl xanthogenates and sulphonates), the substance we have obtained is presumably dibornylene, for which, however, there is no very satisfactory criterion beyond the analytical data. In addition to this liquid a certain amount of a gelatinous material of indefinite boiling point was obtained, but this we have not been able either to purify or identify.

The aqueous layer after the extraction with toluene was strongly acid: by neutralising it with barium carbonate a salt was obtained (Found: Ba, 24·1, 24·15%), showing that the other product of decomposition was naphthalene-β-sulphonic acid.

Bornyl naphthalene-α-sulphonate and bornyl benzenesulphonate distilled under reduced pressure gave the same volatile products, leaving behind naphthalene-α-sulphonic acid and benzenesulphonic acid respectively.

It thus appears that by distilling these sulphonic esters of borneol, a small quantity of camphene and a considerable quantity of dibornylene and a more complex product are obtained, whereas Tschugaev by decomposing bornyl methyl xanthogenate obtained mainly bornylene and a little camphene.

Bornyl naphthalene-β-sulphonate heated in a sealed tube (no

4 M

pressure is developed) at 80—90° for 2—3 hours was completely separated into two layers. On cooling, the lower layer (B) solidified. The upper layer (A) on distillation under reduced pressure gave two fractions, b. p. 60—65°/4 mm. and 140—240°/4 mm. The former on redistillation boiled at 157—160° under ordinary pressure and ultimately solidified; m. p. 85° (Found: C, 86·7, 86·7; H, 13·2, 13·2; *M*, cryoscopic in benzene, 136·8. Calc. for $C_{10}H_{18}$: C, 86·9; H, 13·1%; *M*, 138). The substance did not decolorise bromine and would appear to be dihydrocamphene, since it corresponds closely with the behaviour given for that substance by Vavon (*Compt. rend.*, 1907, **149**, 997) and by Henderson and Pollock (J., 1910, **97**, 1620), and, if Wagner's formula for camphene is accepted, may be presumed to have the formula

$$\begin{array}{lcl} CH_2 - & CH & - CHMe \\ | & CH_2 & | \\ CH_2 - & CH & - CMe_2 \end{array},$$

but no more satisfactory method of identifying this compound seems to be available.

The higher-boiling portion on distillation under reduced pressure gave two fractions, one boiling at 168°/4 mm., and the other, a gelatinous mass which could not be purified or identified, boiling from 240—270°/4 mm. (Found for the former: C, 88·2, 88·2; H, 11·8, 11·8; *M*, cryoscopic in benzene, 268·7. Calc. for $C_{20}H_{32}$: C, 88·2; H, 11·8%; *M*, 272).

Since on decomposition, in sealed tubes, of the corresponding menthyl sulphonates, dimenthene was formed, the above substance is presumably dibornylene. It has the same physical properties as the substance obtained on decomposition by direct distillation.

The strongly acid, solid layer (B) was dissolved in water and boiled with animal charcoal, and a barium salt was precipitated by means of barium chloride and recrystallised from water [Found: Ba, 24·0, 24·15. Calc. for $Ba(SO_3{\cdot}C_{10}H_7)_2,H_2O$: Ba, 24·1%]. The solid is therefore naphthalene-β-sulphonic acid.

Bornyl naphthalene-α-sulphonate and bornyl benzenesulphonate decomposed in a strictly analogous fashion, yielding also what were probably dihydrocamphene, dibornylene, and a gelatinous mass of high boiling point, along with the corresponding sulphonic acid.

Decomposition in Solution.—When bornyl naphthalene-β-sulphonate was heated to boiling in 10% benzene solution for 6 hours there was no change in the rotation of the solution. If, however, toluene was substituted for benzene and the solution heated to 110°, definite decomposition took place and, on cooling, a solid separated. This was acid and gave the characteristic barium salt of naphthalene-α-sulphonic acid. On distillation of the filtrate a liquid, b. p. 285—

290°, or 168°/4 mm., was obtained identical with the high-boiling liquid presumed to be dibornylene.

The two corresponding esters decomposed in the same way, giving dibornylene and the corresponding sulphonic acid, when heated in solution in toluene. Bornyl benzenesulphonate gave a similar result even in boiling benzene.

Hydrolysis of Bornyl Benzene- and Naphthalene-sulphonates.—*d*-Borneol prepared from camphor by reduction contains a considerable proportion of *l*-*iso*borneol which renders the preparation of pure *d*-borneol rather difficult. We found that the bornyl naphthalene-β-sulphonate obtained from commercial *d*-borneol, unlike the naphthalene-α-sulphonate or the benzenesulphonate, could be completely purified by recrystallisation, and it seemed a comparatively simple matter to obtain pure *d*-borneol by hydrolysing the ester thus purified. These bornyl esters, however, cannot be hydrolysed in any of the usual ways, the products obtained being somewhat similar to those got by direct decomposition of the esters.

(1) *Action of water and aqueous potassium hydroxide.* When steam was blown through bornyl naphthalene-β-sulphonate suspended in water or in dilute aqueous caustic potash for 20—30 minutes, only water appeared to distil over and the ester seemed to be practically unchanged.

But when the ester was heated on the water-bath for 2—3 hours with either water or caustic alkali, decomposition took place, and steam now removed a colourless liquid. This did not solidify when separated from the water, and was ethereal in odour. Benzene extracted from it a liquid, b. p. 155—159°, which was optically inactive, gave on analysis results corresponding roughly to the formula $C_{10}H_{16}$, and from its odour seemed to be mostly camphene: it decolorised bromine water. It gave no solid hydrochloride when treated in ether with dry hydrogen chloride, but, on evaporation of the ether, the residue separated into a brown oil and a olourless portion. The latter solidified and had the melting point f camphene hydrochloride. Such camphene as was formed, owever, was apparently mixed with other substances, it being 'ery probable that even if hydrolysis gave different products from he simple heating of the ester the products of hydrolysis were almost ertain, in the circumstances of the experiment, to be mixed with he products due to direct decomposition of the ester by heat. t was not found possible to identify definitely the substances resent, but certainly no borneol was obtained.

(2) *Alcoholic potassium hydroxide.* A solution of bornyl aphthalene-β-sulphonate in a slight excess of alcoholic caustic otash, when heated on the water-bath for several hours, deposited

potassium naphthalene-β-sulphonate. The alcoholic solution was dried with potassium carbonate and most of the alcohol distilled off under reduced pressure. On pouring the residue into water a very small quantity of unchanged ester separated. No borneol was obtained, and we found it impossible completely to identify the products of hydrolysis. All that was noticeable was a strong odour of camphene—a substance extremely difficult to separate from its alcoholic solution.

We attempted this separation by distillation with an efficient fractionating column without success, but, by passing dry hydrogen chloride through the alcoholic solution and adding water, camphene hydrochloride was precipitated; it was rapidly filtered off and crystallised from alcohol containing hydrogen chloride, sufficient being obtained for identification. Any other substances present could not be identified.

In another attempt, the alcoholic solution was poured into a large excess of water, and the whole extracted with toluene, although this did not remove all the camphene. The toluene solution was dried with calcium chloride, and the toluene distilled off under reduced pressure. The main portion of the residue distilled at 155° and formed camphene hydrochloride, but some higher-boiling material had also been formed which could not be satisfactorily identified. The amount of terpene isolated in this manner was about 10% of the theoretical. Experiments to hydrolyse the ester with sodium ethoxide in alcohol and with barium hydroxide in aqueous alcohol were equally unsuccessful, the same products being again indicated. It seems very remarkable that, whereas such esters as bornyl acetate, bornyl *p*-nitrobenzoate (Henderson and Heilbron, P., 1913, 381), bornyl hydrogen phthalate (Pickard and Littlebury, J., 1907, **91**, 1973), and bornyl mandelate (McKenzie and Thompson, J., 1905, **87**, 1013) can easily be hydrolysed in a normal manner, bornyl benzene- and naphthalene-sulphonates decompose in an entirely different fashion, presumably similar to that in which they are decomposed by simple heating.

Hydrolysis of Menthyl Benzene- and Naphthalene-sulphonates.—On account of the peculiarities observed with the bornyl esters we examined also the hydrolysis of the corresponding menthyl derivatives.

(i) *Action of aqueous potassium hydroxide.* When menthyl benzenesulphonate was heated for several hours at about 80—85° with aqueous potassium hydroxide solution (10—15%), decomposition (which was not complete even after 5 or 6 hours) took place and a colourless oil separated. This was distilled over in steam and isolated by means of benzene. It boiled at 165°, gave on analysis

figures corresponding almost exactly to the formula $C_{10}H_{18}$, decolorised bromine, formed a nitrosochloride, m. p. 115°, and was therefore menthene. No side reactions seemed to take place in this case.

Menthene was similarly formed when menthyl naphthalene-β-sulphonate was treated with aqueous potassium hydroxide, but even after heating for 6 hours 50% of the ester was recovered unchanged.

(ii) *Hydrolysis with barium hydroxide.* The three menthyl sulphonates were all decomposed by heating with aqueous-alcoholic solutions of barium hydroxide. The barium salt of the acid was formed almost quantitatively in each case. No menthol, however, could be obtained, but menthene was produced and was extracted from the aqueous-alcoholic solution by toluene; little, if any, of the higher-boiling dimenthene was formed. The decomposition, therefore, with aqueous caustic potash and with alcoholic barium hydroxide is practically identical with the decomposition of the esters when distilled rapidly under reduced pressure.

Temperature of Decomposition in Different Solvents.—From the experiments which have been detailed both here and in connexion with the menthyl esters, it appeared that the decomposition of these sulphonates took place more rapidly in certain solvents than in others, and we thought it worth while to examine this phenomenon systematically. We therefore made up 0·8 g. of ester to 10 c.c. with various solvents and heated the solution for one hour in a thermostat kept at a definite temperature. The solution was then cooled rapidly, diluted with 20 c.c. of absolute alcohol (distilled over quicklime), and titrated with alcoholic potash, a blank experiment being carried out in each case. The results are shown in the table on p. 2470.

It will be observed that not only does increase of temperature cause an increase in the velocity of the reaction, but that there is a great diversity of effect between the different solvents, the rate of increase being much greater in some than in others. The effect of the same solvent on the three esters, however, is, in general, fairly similar. Toluene causes little decomposition in 1 hour at any of the temperatures used, and the alcohols cause considerable decomposition at all temperatures, the percentage increasing with decrease in molecular weight of the alcohol. Although decomposition in the non-alcoholic solvents practically ceases below 85°, it continues to be quite appreciable in the alcohols at considerably lower temperatures. In fact, methyl alcohol at 65° causes more decomposition in a given time than the non-alcoholic solvents at 90—95°. Water would probably show the greatest effect, but this could not be proved owing to the insolubility of these esters even in aqueous-

alcoholic solutions. Nitrobenzene causes little decompositio below 100°, but at 105° decomposition is practically complete i all cases. Ethylene dibromide causes little decomposition i menthyl benzenesulphonate even at 105°, but almost complet decomposition at this temperature in 1 hour in the two naphthalene sulphonic esters.

Percentage of ester decomposed in one hour.

Temp.	C_7H_8.	$C_6H_5{\cdot}NO_2$.	$C_2H_4Br_2$.	C_5NH_5.	$Bu^{\beta}OH$.	$Bu^{\alpha}OH$.	Pr^{α} OH.	EtOH.	MeOH
				Menthyl benzenesulphonate.					
65°	—	—	—	—	—	—	—	3·73	8·95
70	—	—	—	—	—	—	3·17	5·13	—
75	—	—	—	—	·	4·10	5·88	8·73	—
80	—	—	—	—	·	6·77	10·70	—	—
85	0·98	2·37	—	2·37	9·89	10·85	16·42	—	—
90	1·04	2·75	2·48	3·19	16·20	17·27	25·74	—	—
95	1·06	5·88	2·67	4·72	27·17	28·15	38·39	—	—
100	2·23	12·87	4·20	9·80	43·12	45·14	—	—	—
105	2·37	82·15	9·18	14·08	54·44	60·23	—	—	—
				Bornyl naphthalene-β-sulphonate.					
65	—	—	—	—	—	—	—	3·19	8·18
70	—	—	—	—	—	3·12	4·01	6·44	—
75	—	—	—	—	—	5·31	7·12	9·78	—
80	—	—	—	—	—	7·51	10·58	—	—
85	—	—	—	—	—	12·65	15·31	—	—
90	—	6·41	4·39	5·21	17·16	20·90	26·35	—	—
95	—	7·33	6·30	6·36	27·82	31·61	42·03	—	—
100	1·05	71·53	22·90	7·57	39·79	43·92	—	—	—
105	1·06	64·73 (½ hr.)	71·54	11·83	58·27	67·50	—	—	—
				Menthyl naphthalene-β-sulphonate.					
.65	—	—	—	—	—	—	—	4·92	12·9
75	—	—	—	—	—	5·62	8·27	13·53	—
95	1·50	9·30	7·02	6·20	26·96	30·77	41·68	—	—
100	1·50	63·23	28·14	9·11	41·21	45·02	—	—	—
105	1·55	98·63	99·56	13·86	56·13	62·92	—	—	—

EXPERIMENTAL.

l-*Bornyl Benzenesulphonate.*—Pure *l*-borneol (18·5 g.) recrystallise from light petroleum [m. p. 203°, $[\alpha]_{5461}^{17°}$ (benzene, $c = 5·2$ — 42·81°] was dissolved in pyridine (60 g.) and cooled to 0°. Benzen sulphonyl chloride (21·1 g.) was then added very slowly wit constant stirring, the temperature being kept below 3°. Crysta soon began to separate, and on continued stirring became ver abundant. After 3 or 4 hours, a large qnantity of water was adde and ultimately the oil which first separated solidified; it was the filtered off and dried. In several preparations the oil would n solidify in contact with water. It was then extracted with benzen the extract dried with calcium chloride, and the benzene remov by evaporation in air and finally over sulphuric acid in a vacuu desiccator; the residue then solidified to a pale yellow, crystalli mass.

l-*Bornyl benzenesulphonate* is very soluble in all common organic solvents; but may be crystallised from light petroleum, giving fine, white, slightly elongated crystals, m. p. 52°; $[\alpha]_{5461}^{17^\circ}$ in benzene ($c = 2{\cdot}5$) $-$ 22·40°, in alcohol ($c = 2{\cdot}5$) $-$ 22·00°. Several crystallisations are necessary to obtain the substance free from borneol; the yield of pure product is about 25% [Found: S (fusion method), 10·7. $C_{16}H_{22}O_3S$ requires S, 10·95%].

d-*Bornyl benzenesulphonate*, m. p. 52°, is prepared and purified in exactly the same way as the *l*-ester. When prepared from crude *d*-borneol, a product is obtained the rotation of which is lower than that of the pure *l*-compound, + 21·30° (similar conditions), and we were unable to raise it by crystallisation.

l-*Bornyl naphthalene*-β-*sulphonate* was prepared from pure *l*-borneol (18·5 g.) in pure pyridine (90 g.) by means of naphthalene-β-sulphonyl chloride (27·2 g.) in a similar manner to the benzenesulphonate. It is soluble in all the common solvents, but may be recrystallised from methyl or ethyl alcohol, and from light petroleum, from which it separates in stellate masses of glistening, white, needle-shaped crystals. After three crystallisations it has m. p. 76°, and $[\alpha]_{5461}^{17.5^\circ}$ in benzene ($c = 3$) $-$ 16·50° and in alcohol ($c = 2{\cdot}5$) $-$ 16·00°. The yield of pure product is 60% [Found: S (fusion method), 9·2. $C_{20}H_{24}O_3S$ requires S, 9·3%].

d-*Bornyl naphthalene*-β-*sulphonate* was prepared, in exactly the same way as the corresponding *l*-ester, from commercial *d*-borneol, which contains *l*-*iso*borneol. Crystallisation from methyl or ethyl alcohol or light petroleum alone gave a product of m. p. 76°, the rotation of which, however, could not be raised beyond $[\alpha]_{5461}^{17.5^\circ}$ (in benzene, $c = 3$) $-$ 15·8°. But after the ester had been crystallised twice from a *mixture* of methyl alcohol and light petroleum the rotation rose to the value found for the *l*-ester.

l-*Bornyl naphthalene*-α-*sulphonate* was prepared and isolated in the way described for *l*-bornyl benzenesulphonate, naphthalene-α-sulphonyl chloride (27·2 g.) being used. The substance was difficult to purify owing to its great solubility, but after three to six recrystallisations from light petroleum it was obtained in fine, white crystals, m. p. 90°, $[\alpha]_{5461}^{17.5^\circ}$ in benzene ($c = 2{\cdot}5$) $-$ 23·20° and in alcohol ($c = 2{\cdot}5$) $-$ 26·4° (Found: S, 9·2. $C_{20}H_{24}O_3S$ requires S, 9·3%).

The corresponding *d*-ester was prepared from crude *d*-borneol but could not be completely purified.

Summary.

Menthyl esters of benzene-, naphthalene-α- and naphthalene-β-sulphonic acids, when directly distilled under reduced pressure, yield menthene and the corresponding sulphonic acid; but if they

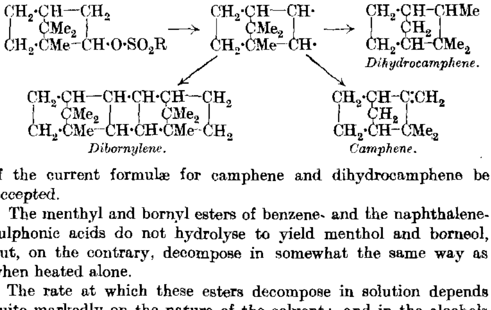
are heated for some time before distillation, dimenthene and more complex substances are produced, but no menthene.

The corresponding bornyl esters, when directly distilled, yield camphene, dibornylene, a more complex gelatinous material which we have been unable to purify or identify, and sulphonic acid.

The bornyl esters, when heated for 2 or 3 hours and then distilled, yield dihydrocamphene, dibornylene, a gelatinous material, and sulphonic acid.

The bornyl esters, heated to boiling in toluene solution, yield dibornylene and the corresponding sulphonic acid.

These changes may be represented thus :—



if the current formulæ for camphene and dihydrocamphene be accepted.

The menthyl and bornyl esters of benzene- and the naphthalene-sulphonic acids do not hydrolyse to yield menthol and borneol, but, on the contrary, decompose in somewhat the same way as when heated alone.

The rate at which these esters decompose in solution depends quite markedly on the nature of the solvent; and in the alcohols the velocity increases rapidly as the molecular weight diminishes. Tables are given showing this behaviour.

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CCCXXVII.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XXV. Bornyl Benzene- and Naphthalene-sulphonates in Various Solvents.*

By THOMAS STEWART PATTERSON and IRENE MARY MCALPINE.

WE have examined the rotations of the esters described in the foregoing paper for three colours of light, mercury yellow ($\lambda = 5790$), mercury green ($\lambda = 5461$), and mercury violet ($\lambda = 4358$), in several

of the alphabet, namely, (*a*) ethyl alcohol, (*b*) benzene, (*c*) pyridine, (*d*) ethylene dibromide, (*e*) quinoline, (*f*) nitrobenzene. Only one solution was examined in each case at a concentration between 2·5 and 3·5. The data are given in Table I.

TABLE I.

Specific Rotations of Bornyl Sulphonates in Various Solvents.

t = approximately 17·5° throughout.

Solvent.	*a*.	*b*.	*c*.	*d*.	*e*.	*f*.
Concentration	2·5	3·0	3·5	3·5	3·5	3·5
	l-Bornyl naphthalene-β-sulphonate.					
Yellow	−14·00°	−14·25°	−14·99°	−19·43°	−17·29°	−13·14°
Green	16·00	16·50	17·28	22·43	20·00	15·14
Violet	26·40	27·17	28·56	37·14	33·14	25·14
	l-Bornyl benzenesulphonate.					
Yellow	−19·00	−19·98	−21·84	−25·60	−26·56	−18·85
Green	22·00	23·15	24·84	29·43	30·57	21·74
Violet	36·40	38·30	41·13	49·00	51·13	36·00
	l-Bornyl naphthalene-α-sulphonate.					
Yellow	−22·80	−20·51	−18·14	−26·28	−27·14	−20·00
Green	26·40	23·50	20·71	30·00	31·14	22·83
Violet	43·60	38·80	34·11	49·57	51·43	38·28

The rotations vary considerably in each case with change of solvent. Bornyl naphthalene-β-sulphonate has the lowest rotation values except for the solution in ethylene dibromide, which overlaps some of the values for other esters. The rotations of the other two esters in the different solvents overlap each other completely, the range of variation being greater, however, with the naphthalene-α-sulphonate than with the benzenesulphonic ester. The different solvents do not influence the rotations in the same way, although there are resemblances. Quinoline, which usually has a powerful exalting or depressing influence, produces the highest rotation in bornyl naphthalene-α-sulphonate and in bornyl benzenesulphonate, and the second highest rotation in bornyl naphthalene-β-sulphonate. In ethylene dibromide, which generally has a powerful influence in the opposite direction to quinoline, bornyl naphthalene-β-sulphonate shows the highest rotation and the other two the second highest. Nitrobenzene produces the lowest rotation in bornyl naphthalene-β-sulphonate and in bornyl benzenesulphonate, and the second lowest in bornyl naphthalene-α-sulphonate. The lowest rotation of this ester is produced by pyridine. There is thus some similarity in the action of the same solvent on the three esters.

The values obtained for the rotation of the three esters in the various solvents were plotted on a characteristic diagram, and lay with good agreement along lines intersecting one another very near

the point of origin of the diagram. It therefore follows that the dispersion coefficients for all these compounds, calculated by the ordinary method, ought to be the same throughout. This is seen by Table II to be roughly the case.

TABLE II.

Dispersion Ratios.

	Bornyl benzene-sulphonate.		Bornyl naphthalene-α-sulphonate.		Bornyl naphthalene-β-sulphonate.	
Solvent.	Hg_v/Hg_g.	Hg_y/Hg_g.	Hg_v/Hg_g.	Hg_y/Hg_g.	Hg_v/Hg_g.	Hg_y/Hg_g.
Alcohol	1·655	0·864	1·625	0·875	1·651	0·863
Benzene	1·654	0·863	1·646	0·863	1·650	0·873
Pyridine	1·655	0·879	1·652	0·868	1·647	0·876
Ethylene dibromide ...	1·665	0·868	1·656	0·866	1·652	0·876
Quinoline ...	1·683	0·878	1·658	0·864	1·667	0·871
Nitrobenzene	1·655	0·867	1·661	0·868	1·675	0·875

This property seems to be characteristic of bornyl and menthyl esters. Indeed the characteristic diagrams for the bornyl sulphonic esters and the menthyl sulphonic esters nearly coincide. Kenyon and Pickard have found (J., 1915, **107**, 35) that most menthyl derivatives lie on the same characteristic diagram with dispersion coefficient mercury violet/mercury green 1·634 to 1·675. The menthyl sulphonic esters have approximately the same coefficient, and lie on the same diagram. The bornyl esters that they plotted had as coefficient V/G = 1·707 to 1·871. The sulphonic esters that *we have investigated, however, do not lie on this diagram, but on* that which contains the majority of the menthyl compounds.

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CCCXXVIII.—*Equilibrium in the Binary Systems Cresols–Amines.*

By NIKOLAI ANTONOVITCH PUSHIN and LJUDEVIT SLADOVIĆ.

IN this paper equilibrium diagrams are described which were obtained from thermal analysis of mixtures of *o*-, *m*-, or *p*-cresol, on the one hand, and dimethylaniline, *p*-toluidine, quinoline, piperidine, 1 : 5-naphthylenediamine, or carbamide, on the other. For every mixture the following data were determined : (1) the temperature of

complete melting of the crystallised mixture; (2) the complete cooling curve; (3) the duration of the eutectic crystallisation.

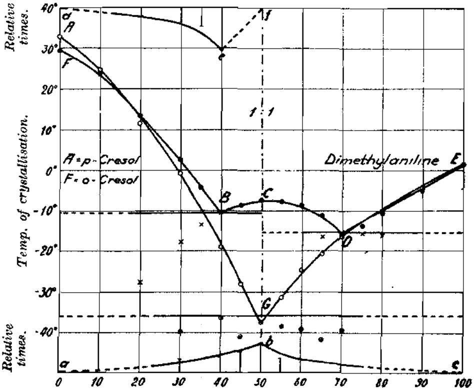
In the tables the temperature I is that of primary crystallisation, and II that of the eutectic (or final) crystallisation. The temperature III, when given, refers to complete melting of the mixture, and IV (for *o*-cresol and carbamide only) is the transition temperature.

TABLE I.

o-Cresol–Dimethylaniline (Fig. 1).

$C_6H_5{\cdot}NMe_2$, mols. %.	Temp. I.	Temp. II.	$C_6H_5{\cdot}NMe_2$, mols. %	Temp. I.	Temp. II.
0	29·5°	—	55	− 7·7°	—
10	23·8	—	60	− 8·5	—
20	13·5	−27·6°	65	−11·2	−16·2°
30	2·5	−17·7	70	—	−15·6
35	− 4·1	−13·5	75	−13·7	−16
40	—	−10·5	80	−10·7	−16·2
45	− 8·6	—	90	− 5	—
50	− 7·4	—	100	+ 1·6	—

FIG. 1.



Mols. % of dimethylaniline in {o-*cresol* + *dimethylaniline* · · · *and* × × ×; p-*cresol* + *dimethylaniline* ○ ○ ○ *and* ⊙ ⊙ ⊙}

o-*Cresol–Dimethylaniline*.—The diagram is composed of three parts and is characterised by two eutectic points with one open maximum at 50 mol.% of each component, showing the formation of

a definite *compound* of equimolecular composition, m. p. −6°. The two eutectics *B* and *D* correspond to 40 mols.% (at −9°) and 70 mols.% (at −14°) of dimethylaniline respectively. The triangle *def* shows the relative duration of crystallisation at and near the first eutectic point.

TABLE II.

p-Cresol–Dimethylaniline (Fig. 1).

$C_6H_5{\cdot}NMe_2$, mols. %.	Temp. I.	Temp. II.	$C_6H_5{\cdot}NMe_2$, mols. %.	Temp. I.	Temp. II.
0	33°	—	55	−31·3°	−38·4°
10	24·6	—	60	−24·8	−39·3
20	11·7	—	65	−20·7	−41·7
30	−0·8	−39·8°	70	−16·4	−39·4
40	−19	−36·2	80	−10·2	—
45	−28	−41	90	−5	—
50	—	−37·2	100	+1·6	—

p-Cresol–Dimethylaniline.—Both the cooling curves and the temperatures of definite melting of the mixtures lead to the conclusion that *p*-cresol does not form a definite compound with dimethylaniline but only mechanically mixed crystals. The diagram is composed of two arms intersecting in the eutectic point (50 mols.% and −35°), the position of which is confirmed by the triangle *abc* for the duration of crystallisation.

TABLE III.

o-Cresol–*p*-Toluidine (Fig. 2).

$C_7H_7{\cdot}NH_2$, mols. %.	Temp. I.	Temp. II.	$C_7H_7{\cdot}NH_2$, mols. %.	Temp. I.	Temp. II.	$C_7H_7{\cdot}NH_2$, mols. %.	Temp. I.	Temp. II.
0	30·3°	—	30	21·4°	12·9°	75	—	24·8°
10	23	—	40	32·8	—	80	31°	25·6
15	19·2	14°	50	38	—	90	37·3	22·5
20	—	14	60	34	22·2	100	43·5	—
25	17·6	13·8	70	26·5	24·5			

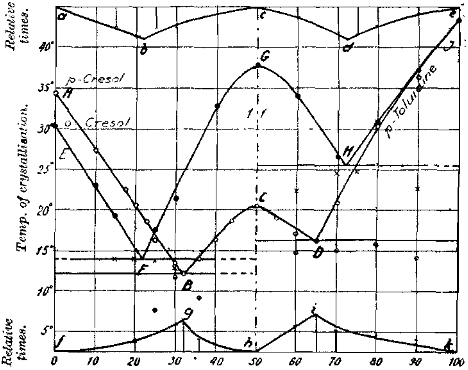
TABLE IV.

p-Cresol–*p*-Toluidine (Fig. 2).

$C_7H_7{\cdot}NH_2$, mols. %.	Temp. I.	Temp. II.	$C_7H_7{\cdot}NH_2$, mols. %.	Temp. I.	Temp. II.	$C_7H_7{\cdot}NH_2$, mols. %.	Temp. I.	Temp. II.
0	34·4°	—	32	—	12·1°	60	17·1°	14·8°
10	27·3	—	36	14°	9·1	65	—	16·4
17·5	22·5	—	40	16·4	—	70	20·9	15
20	20·6	3·8°	44	18·6	—	80	30·4	15·8
23	18·6	—	50	20·5	—	90	37·4	14·1
25	16·3	7·6	55	19·1	—	100	43·5	—
30	13·4	11·7						

o-*Cresol*–p-*Toluidine and* p-*Cresol*–p-*Toluidine*.—These two systems give very similar diagrams, each consisting of three sections and two eutectic points with one open maximum between them which corresponds to 50 mols.% of each component. Hence each pair forms an equimolecular *compound* of m. p.'s 38° and 20·5°, respectively, melting being without decomposition in each case. In the system *o*-cresol–*p*-toluidine the eutectic points are at 22 and 72 mols.% of *p*-toluidine, and 14° and 25·6°, and in the other system at 32 and 65 mols.% and 12·1° and 16·4°. The duration of eutectic

FIG. 2.



Mols. % of p-*toluidine in* {o-*cresol* + p-*toluidine* · · · *and* × × ×; p-*cresol* + p-*toluidine* ○ ○ ○ *and* ⊙ ⊙ ⊙}

crystallisation of different mixtures (triangles *abc*, *cde*, *fgh*, *hik*) confirms the position of the eutectic points.

Although *o*-cresol melts at a lower temperature (30·3°) than *p*-cresol (34·4°), yet in the equimolecular compounds with *p*-toluidine there is a difference of 18·5° in the reverse direction. If it be assumed that a greater change in physical properties corresponds to a deeper change in the chemical nature and to greater stability of a newly-formed compound, then it follows that the *o*-cresol compound is more stable than its isomeride.

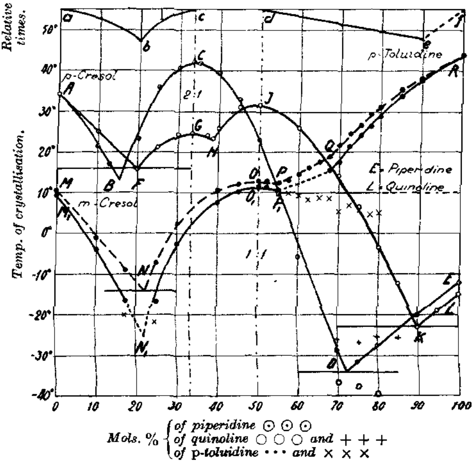
m-*Cresol*–p-*Toluidine*.—In this system the temperature of primary crystallisation is given as well as the temperature of melting of the last crystals. The first curve is shown by a continuous and the

TABLE V.

m-Cresol–*p*-Toluidine (Fig. 3).

$C_7H_7·NH_2$, mols. %.	Temp. I.	Temp. II.	Temp. III.	$C_7H_7·NH_2$, mols. %.	Temp. I.	Temp. II.	Temp. III.
0	+ 9·4°	—	10·4°	62·5	—	8·2°	16°
10	− 3·9	—	− 1·0	65	—	8·6	17·4
17·5	−16·4	−20°	− 9	67·5	15·5°	8·5	18·9
25	−16·7	−21·7	− 7·3	70	17·5	5·2	21·7
30	− 2·5	—	+ 2·5	72·5	21·5	6·9	24·7
40	+ 7·7	—	10·6	75	24	5·8	26·7
45	10·1	—	12	77·5	26·2	4·4	29·3
50	11·8	—	12·9	80	28·6	5	31
52	11·5	—	12·9	85	33·7	—	35·1
55	10·7	—	12·2	90	37·2	—	38
57·5	—	9·7	13·0	100	43·5	—	—
60	—	9·1	14·8				

FIG. 3.



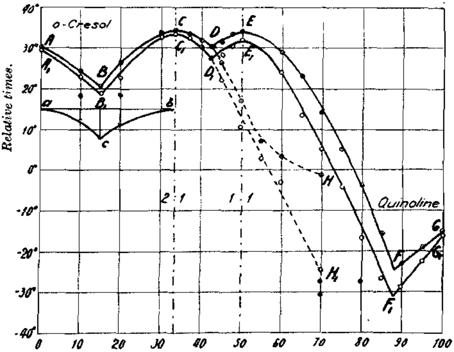
second by a broken line (Fig. 3); the two are almost parallel, bu the upper curve (complete melting) gives more definite results tha the other because in the ranges 17·5—25 and 55—67·5 mols.% c *p*-toluidine it has not been possible to determine the temperature c the primary crystallisation, owing to the slowness of crystallisatio

TABLE VI.

o-Cresol–Quinoline (Fig. 4).

C_9H_7N, mols. %.	Temp. I.	Temp. II.	Temp. III.	C_9H_7N, mols. %.	Temp. I.	Temp. II.	Temp. III.
0	29·5°	—	30·3°	50	32°	—	34·2°
10	23	18·6°	24·4	55	2·8	—	7
15	18·7	18·7	20·7	60	− 3	—	+ 3·5
20	22·8	18·5	26·6	60	+24·1	—	+29
30	32·8	—	34	65	+13·5	—	23
33·3	33·5	—	34·5	70	−24·5	−30·7°	− 1·2
37	32·5	—	33·7	70	+ 5	−27·4	+14
40	30·1	—	32	75	− 4·3	—	+ 5
42·5	—	27·2	30·5	80	−16·7	−27·7	− 4
45	22	—	26·4	85	−26·4	—	−15·5
45	28·3	—	31·7	90	−28·7	—	−22·8
47·5	30·7	—	33·4	95	−22·3	—	−19
50	10·5	—	17	100	−16	—	−15

FIG. 4.



Mols. % of quinoline.

and to the proximity to the eutectic point. The positions of the eutectic points N_1 and P_1 can therefore be determined only approximately, but the eutectic point N lies at 22 mols.% of *p*-toluidine and −14°, and P at 56 mols.% and 12°. The maximum at O corresponds to an equimolecular *compound*.

There appears to be a break in the curve at 67 mols.% of *p*-toluidine, and on the cooling curves there is a slight change of

direction, corresponding to a heat effect, at 72·5—80%; no significance can be attached to these, however.

o-*Cresol–Quinoline.*—For this system the cooling curve, ($A_1B_1C_1D_1E_1F_1G_1$) *and the temperatures of complete melting of* crystalline mixtures (curve *ABCDEFG*) have been determined (see Fig. 4). These curves are very similar, but in places they are separated by 12°.

The diagram is composed of four sections giving two open maxima at *C* and *E*, corresponding to *compounds* $C_9H_7N,2C_7H_7{\cdot}OH$ (m. p. 34·5°) and $C_9H_7N,C_7H_7{\cdot}OH$ (m. p. 34·2°). Two eutectics are at *15 and 88 mols.% of quinoline and 20° and —24° respectively.*

The lines *DH* and D_1H_1 represent a metastable state of the ternary and not of the binary compound, for (1) they are continuations of the curves *CD* and C_1D_1, and (2) every temperature of crystallisation of the mixture along the curve D_1H_1 corresponds to a temperature along the curve *DH*, where the whole mixture is in a liquid state, whereas the crystals of the binary compound melt only at temperature shown by the curve *DEF*.

TABLE VII.

p-Cresol–Quinoline (Fig. 3).

C_9H_7N, mols. %.	Temp. III.	Temp. II.	C_9H_7N, mols. %.	Temp. III.	Temp. II.	C_9H_7N, mols. %.	Temp. III.	Temp. II.
0	34·4°	—	38·5	23·2°	—	75	6·3°	−27·2°
10	25·0	6·7°	40	26	—	80	− 3·3	−24·8
20	16	—	45	31	—	85	−12·3	−25·4
25	21·2	4	50	31·8	—	90	−23	−26
30	24·4	—	60	26	—	95	−19	—
33·3	24·5	—	70	14	−25·6°	100	−15	—
37	24·2	—						

p-*Cresol–Quinoline.*—The diagram of this system is very similar to that of the system *o*-cresol–quinoline, showing two open maxima corresponding to the *compounds* $C_9H_7N,C_7H_7{\cdot}OH$ and $C_9H_7N,2C_7H_7{\cdot}OH$ of m. p. 31·8° and 24·5° respectively. Two well-defined eutectic points are at 20 and 90 mols.% of quinoline and 16° and −23°, respectively; these have been confirmed by the duration of crystallisation (triangles *abc* and *def*). The minimum at 38·5 *mols.*% may not be a true eutectic, for it has not yet been ascertained whether a series of solid solutions is formed.

Comparison of the diagrams for the systems o-cresol–quinoline and *p*-cresol–quinoline shows that the curves of the first system are higher than those of the second, almost throughout. Both cresols therefore behave towards quinoline just as towards *p*-toluidine except that with quinoline they form not one but two definite compounds.

TABLE VIII.

p-Cresol–Piperidine (Fig. 3).

$C_5H_{11}N$, mols. %.	Temp. III.	$C_5H_{11}N$, mols. %.	Temp. III.	Temp. II.
0	34·4°			
5	29·5	45	33°	—
10	21·5	50	23	—
13	17·0	55	9·7	—
20	23·5	60	− 5·6	—
25	36	70	−28·6	−36·7°
30	40·9	75	−31·7	−37·7
33·3	42·1	80	−27·5	−39·5
35	41·9	90	−20	—
40	39·5	100	−12	—

p-*Cresol–Piperidine.*—The diagram consists of three sections showing two eutectic points and one open maximum, which corresponds to the *compound* $C_5H_{11}N,2C_7H_7{\cdot}OH$, m. p. 42·1°. The eutectics are at 15·5 and 72 mols.% of piperidine (14° and −34°, respectively), the former having been determined by interpolation because within 13—20 mols.% and 60—70 mols.% of piperidine we were unable to make the mixtures crystalline. It is noteworthy that *the above compound does not correspond to piperidine as mono-acid* base and to *p*-cresol as monobasic phenol.

TABLE IX.

p-Cresol–1 : 5-Naphthylenediamine (Fig. 5).

$C_{10}H_6(NH_2)_2$, mols. %.	Temp. I.	Temp. II.	$C_{10}H_6(NH_2)_2$, mols. %.	Temp. I.	Temp. II.
0	33°	—	37	119·2°	118°
5	31·6	—	40	125	116·5
10	—	29°	45	128·2	116·1
13	106	28·7	50	136·5	111
15	109	—	60	145	107·8
15·8	110	13·5	70	154·6	86·7
20	114·2	—	80	164·1	—
25	116·9	—	90	170·5	—
33·3	118	—	100	189	—

p-*Cresol*–1 : 5-*Naphthylenediamine.*—From naphthylenediamines as diacid bases one might have expected the formation of compounds *with p-cresol of the type* $C_{10}H_6(NH_2)_2,2C_7H_7{\cdot}OH$, *and this is actually* found.

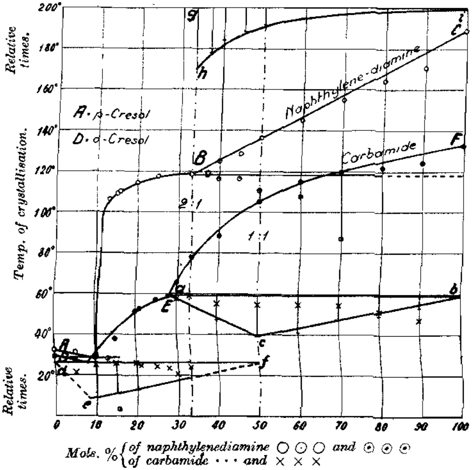
The diagram is composed of three sections and is characterised by one eutectic point at 10 mols.% of naphthylenediamine and 29° and by one transition point at 33 mols.% of naphthylenediamine and 118°. For the determination of the composition of the compound the duration of crystallisation at the transition temperature was studied (triangle *ghi*), and showed a maximum at 33·3 mols.% of naphthylenediamine.

TABLE X.

o-Cresol–Carbamide (Fig. 5).

$CO(NH_2)_2$, mols. %.	Temp. I.	Temp. II.	Temp. IV.	$CO(NH_2)_2$, mols. %.	Temp. I.	Temp. II.	Temp. IV.
0	29·5°	—	—	33·3	78°	24°	58·3°
5	27·4	21·2°	—	40	88·2	—	55
10	29·9	25·1	—	50	105	—	56
15	38	25·9	—	60	115	—	55
20	51·7	26·1	—	70	120	—	54
21	53	25·1	—	80	122	—	51·3
25	57·2	24·4	—	90	124·5	—	47
28	59	22·6	59°	100	133	—	—
30	66	20·5	56·9				

FIG. 5.



o-*Cresol–Carbamide*.—According to Philip (J., 1903, **83**, 814) an Kremann and Rodinois (*Monatsh.*, 1906, **27**, 138), 1 mol. of carbamid forms compounds with 2 mols. of phenol, and with 1 mol. of eac cresol (Kremann, *ibid.*, 1907; **28**, 1125), but Kremann studied onl

the temperature of first crystallisation and not that of definite crystallisation of the mixtures. He determined the composition of the compounds by analysis. We have now investigated complete cooling curves of all mixtures, and have confirmed Kremann's results.

The diagram of this system consists of three sections and is characterised by a eutectic point at 8 mols.% of carbamide and 26°, and by a transition point at 28 mols.% of carbamide and 59°, corresponding to the dissociation of the compound $C_7H_7·OH,CO(NH_2)_2$ into its components. The composition was determined by the duration of crystallisation at the temperature of formation (triangle *abc*) and at the eutectic temperature (triangle *def*). The maximum duration is shown for the equimolecular mixture.

Summary.

The diagrams of ten binary systems have been constructed for the cresols with certain bases, and the existence of the following compounds has been demonstrated :

$C_6H_5·NMe_2$,*o*-$C_6H_4Me·OH$	C_9H_7N,*o*-$C_6H_4Me·OH$	$C_5H_{11}N$,2*p*-$C_6H_4Me·OH$
p-$C_6H_4Me·NH_2$,*o*-$C_6H_4Me·OH$	C_9H_7N,2*o*-$C_6H_4Me·OH$	1 : 5-$C_{10}H_6(NH_2)_2$,2*p*-$C_6H_4Me·OH$
p-$C_6H_4Me·NH_2$,*m*-$C_6H_4Me·OH$	C_9H_7N,*p*-$C_6H_4Me·OH$	$CO(NH_2)_2$,*o*-$C_6H_4Me·OH$
p-$C_6H_4Me·NH_2$,*p*-$C_6H_4Me·OH$	C_9H_7N,2*p*-$C_6H_4Me·OH$	

All except the last melt without decomposition.

Dimethylaniline and *p*-cresol form only mechanical mixtures.

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[*Received, May 4th,* 1928.]

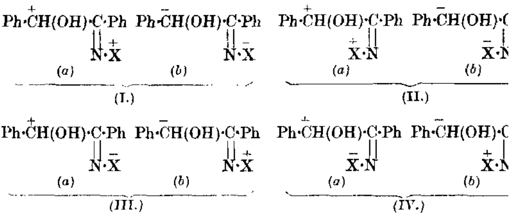
CCCXXIX.—*A Resolution of Benzoin.*

By ISAAC VANCE HOPPER and FORSYTH JAMES WILSON.

IN a previous paper (J., 1922, **121**, 866) it was pointed out that *d*-δ-(α-phenylethyl)semicarbazide, $NH_2·NH·CO·NH·CHMePh$, of which we prepared the hydrochloride, should prove of service in resolving racemic aldehydes and ketones. We have now prepared also the *hydrochloride* of the l-*isomeride*, and by means of these reagents have succeeded in isolating the *d*- and *l*-forms of benzoin.

In order to gain experience of the semicarbazones involved, we decided first to experiment with the racemic semicarbazide both in pyridine and alcoholic solution. Since with *r*-benzoin-δ-(α-phenyl-

ethyl)semicarbazone stereoisomerism of the Hantzsch–Werner typ is possible, four racemic modifications should exist (+ = *d*, − = *l*)



$\overset{+}{X}$ = NH·CO·NH·$\overset{+}{C}$HMePh $\overset{-}{X}$ = NH·CO·NH·$\overset{-}{C}$HMePh

The reaction between benzoin and *r*-δ-(α-phenylethyl)semicarb azide hydrochloride took place smoothly in pyridine solution an three of the four possible *compounds* were obtained, the α-modific ation melting at 174°, the β- at 154°, and the γ- (obtained in ver small quantity) at 137°: each of these gave benzoin on hydrolysi with acid. The reaction proceeded much less conveniently ir *alcoholic solution, the α- and β-modifications in addition to som* unaltered benzoin being obtained—a result which was somewhat unexpected, since previous experiments (J., 1925, **127**, 1282) had shown that as a rule only one modification of a benzoin-semicarbazone was obtained when working in alcoholic solution. It was decided therefore to employ pyridine as solvent in attempting a resolution of benzoin.

An optically active semicarbazide has not hitherto been successfully employed in a resolution: Forster and Fierz (J., 1905, **87**, 722) prepared camphoryl-ψ-semicarbazide, but do not appear to have used it for this purpose. Other active derivatives of hydrazine have, however, been employed for the resolution of *r*-arabinose (Neuberg, *Ber.*, 1903, **36**, 1192) and of *r*-arabinose and *r*-galactose (Neuberg and Federer, *Ber.*, 1905, **38**, 868). Benzoin itself does not appear to have been previously resolved, although the two enantiomorphs have been synthesised (McKenzie and Wren, J., 1908, **93**, 809; Wren, J., 1909, **95**, 1583).

By combining *r*-benzoin with *d*-δ-(α-phenylethyl)semicarbazide four active modifications of the semicarbazone are possible, *viz.*, *Ia*, *IIa*, *IIIb*, and *IVb*. When combination was effected in pyridine solution, however, only one product was obtained in a crystalline condition, the others being oily and very soluble. This lævorotatory

substance, a d-δ-(*α-phenylethyl*)*semicarbazone* of *d*-benzoin, agreed in rotation and m. p. with the product obtained by condensing the *d*-semicarbazide with *d*-benzoin (prepared according to McKenzie and Wren, *loc. cit.*). Hydrolysis of this semicarbazone in aqueous solution with oxalic acid liberated *d*-benzoin. In the same way, from the *l*-semicarbazide hydrochloride and *r*-benzoin, we isolated a dextrorotatory *semicarbazone* which yielded *l*-benzoin on hydrolysis.

EXPERIMENTAL.

Benzoin and r-δ-(*α-Phenylethyl*)*semicarbazide Hydrochloride*.—(a) *In pyridine solution*. Solutions of 8 g. of benzoin (1 mol.) in 80 c.c. of pyridine and 8·1 g. (1 mol.) of the hydrochloride in 100 c.c. of water were mixed in the cold, kept for 6 days, and poured into a large volume of cold water: the sticky product, which would not solidify, was collected, dissolved in ether, the ethereal solution shaken with water to remove pyridine, decolorised with animal charcoal, and filtered hot. In a few hours a product (Crop I) began to separate, and was collected after 2 days. Whilst it was difficult to obtain further solid matter from the filtrate, gradual addition of light petroleum during 2 days precipitated a coloured product, which was filtered and washed with ether until colourless (Crop II). Further gradual addition of light petroleum during a few weeks deposited a small crop (Crop III) which was collected and washed as before. Crop I was recrystallised successively from ether, benzene, and alcohol (the solubility increasing in this order of solvents), from which long, colourless needles (4 g., m. p. 154°) of *benzoin-δ-(α-phenylethyl)semicarbazone* (β-modification) were deposited (Found: N, 11·19. $C_{23}H_{23}O_2N_3$ requires N, 11·26%). Crop II, which was less soluble in the usual organic solvents, dissolved completely on prolonged boiling with benzene, and a fine, amorphous product separated on cooling. This crystallised from alcohol in prisms (3 g., m. p. 174°) of the *α-modification* of the semicarbazone (Found: N, 11·26%). These two stereoisomerides, a mixture of which melted at 140—145°, both gave benzoin on hydrolysis with either hydrochloric or oxalic acid. Crop III was separated by ether into a less soluble (β-modification) and a more soluble fraction. The latter on recrystallisation from a mixture of ether and light petroleum gave long, woolly needles (0·4 g., m. p. 187°) of the *γ-modification* (Found: N, 11·37%) which gave benzoin on hydrolysis with hydrochloric acid. The colouring matters produced in the reaction had a marked effect on the solubilities of the substances.

(b) *In alcoholic solution*. 4 G. of benzoin in 300 c.c. of alcohol were mixed in the cold with 4 g. of the semicarbazide hydrochloride in a little water. After standing for 6 days, dilution with much

cold water gave a soft, but filterable, precipitate which was collected and dissolved in the minimum of boiling alcohol. The crystals deposited on cooling were fractionally recrystallised from ether; a little benzoin separated first and was removed, then a mixture of needles and prisms appeared. On reheating the mixture in the mother-liquor, the needles redissolved so much more quickly that it was possible to effect a fairly complete separation of the prisms by filtering the hot solution at the appropriate moment. The prisms on recrystallisation from alcohol proved to be the α-isomeride, m. p. 174°. The ethereal mother-liquor on standing gave needles, mixed with a small quantity of prisms which were separated by reheating and filtering. The warm filtrate diluted with two volumes of light petroleum deposited crystals which, after purification from alcohol, proved to be the β-isomeride, m. p. 154°.

1-δ-(α-*Phenylethyl)semicarbazide Hydrochloride.*—26·3 G. of *l*-α-phenylethylamine ($[\alpha]_D^{16^\circ}$ − 41·48°, prepared by a combination of the methods of Lovén and Betti: see Hopper and Ritchie, *J. Roy. Tech. Coll.*, 1926, **3**, 65) and 25 g. of acetonesemicarbazone were heated in a bath at 135—138° for 30 minutes under reflux, and then for a further 30 minutes without the condenser. The product, poured into 200 c.c. of ice-water, solidified on standing for a short time. The acetone-*l*-δ-(α-phenylethyl)semicarbazone was collected and hydrolysed by heating with 5% hydrochloric acid (1 mol., calculated on acetonesemicarbazone used) for 2·5 hours on a boiling water-bath, acetone being thus expelled. On cooling, an amorphous solid—probably a derivative of carbamide—was removed, the filtrate was concentrated under reduced pressure (which increases the yield), and the 1-δ-(α-*phenylethyl)semicarbazide hydrochloride* allowed to crystallise out in a number of crops so that the heating of very concentrated solutions was avoided. On recrystallisation from boiling absolute alcohol, 36·5 g. (79% yield) of the hydrochloride were obtained; m. p. 188°; $\alpha_D^{12 \cdot 2^\circ}$ −4·00°, $[\alpha]_D^{12 \cdot 2^\circ}$ − 66·06° (c = 3·027 in water; l = 2).

Synthesis of d-*Benzoin*-d-δ-(α-*phenylethyl)semicarbazone.*—*d*-Benzoin was synthesised from *d*-mandelic acid by Wren's method (*loc. cit.*) with certain modifications suggested to us by Professor McKenzie and Dr. Roger, to both of whom we are much indebted for advice in this connexion. The *d*-mandelamide was prepared from methyl *d*-mandelate by the method of McKenzie and Smith (J., 1922, **121**, 1358). In this and in subsequent preparations and recrystallisations, quartz vessels were employed and solvents were distilled in quartz before use. It was found more convenient to recrystallise *d*-benzoin from a mixture of alcohol and light petroleum than from alcohol alone. The *d*-benzoin melted at 133—134°; $\alpha_D^{11^\circ}$ + 4·47°,

$[\alpha]_D^{14°}$ + 118·5° (c = 0·9433 in acetone; l = 4); a solution in freshly distilled pyridine showed no alteration in specific rotation ($[\alpha]_D^{15°}$ + 92·8°; c = 1·040; l = 1) on standing for a week in a quartz apparatus. *d*-Benzoin is therefore not racemised by pyridine under these conditions.

A mixture of 1·1 g. of *d*-benzoin, dissolved in 67 c.c. of pyridine, with 1·3 g. of *d*-δ-(α-phenylethyl)semicarbazide hydrochloride, dissolved in 2·5 c.c. of water, deposited crystals of the d-δ-(*α-phenylethyl*)*semicarbazone* of *d*-benzoin when left for 6 days. These were collected, and the filtrate, when worked up as described for the reaction product obtained in the resolution (below) yielded some more; two recrystallisations from absolute alcohol gave needles (0·5 g.), m. p. 181—182°, $\alpha_D^{14°}$ − 2·405°, $[\alpha]_D^{14°}$ − 140·7° (c = 0·4274 in absolute alcohol; l = 4) (Found: N, 11·30. $C_{23}H_{23}O_2N_3$ requires N, 11·26%). Further recrystallisation failed to alter the specific rotation.

Resolution of Benzoin.—(1) *By means of* d-δ-(*α-phenylethyl*)*semicarbazide hydrochloride.* 9 G. of the semicarbazide hydrochloride, dissolved in 18 c.c. of water, were added to a solution of 8 g. of benzoin in 70 c.c. of pyridine at 18°, and the mixture after standing for 7 days was poured into 1000 c.c. of cold water. In about 80 minutes the opalescent liquor was decanted from the thick, sticky oil, and the latter was agitated three times with almost boiling water, with cooling and decanting each time. The hard, glassy solid thus obtained (and the beaker containing it) were exposed for 72 hours in an evacuated desiccator over sulphuric acid to remove the last traces of pyridine and water. A solution of the product in about 50 c.c. of pure dry ether deposited a crop of crystals on standing a few hours or on addition of light petroleum. (The ethereal mother-liquor, after various attempts to recover material from it, gave only a gummy product.) The crystals were collected, washed with ether, and recrystallised twice from boiling absolute alcohol, in which the compound was sparingly soluble when cold. The *d*-δ-(α-phenylethyl)semicarbazone of *d*-benzoin thus obtained was optically pure (repeated recrystallisation from alcohol failing to raise its specific rotation) and consisted of needles, m. p. 181—182°; yield 1·8 g. (Found: N, 11·29%); $\alpha_D^{14°}$ − 2·415°, $[\alpha]_D^{14°}$ − 141·5° (c = 0·4268 in absolute alcohol; l = 4). It showed no lowering of m. p. on admixture with the product (m. p. 181—182°) obtained from synthetic *d*-benzoin; the appearance of both was identical under the microscope, and the specific rotations (− 140·7° and − 141·5°) are identical within the limits of experimental error.

(2) *By means of* l-δ-(*α-phenylethyl*)*semicarbazide hydrochloride.* Using 13·2 g. of the *l*-semicarbazide hydrochloride in 26 c.c. of water, and 12·5 g. of benzoin in 95 c.c. of pyridine, and working up the

product as in the last preparation, we obtained 1·8 g. of pure l-*benzoin*-l-δ-(*α-phenylethyl*)*semicarbazone*, m. p. 181—182° (Found : N, 11·32%). The product was optically pure after two recrystallisations from absolute alcohol, in which $\alpha_D^{14°} = + 4·40°$, $[\alpha]_D^{14°} + 140·9°$ ($c = 0·7808$; $l = 4$).

Liberation of d- *and of* l-*Benzoin*—(1) d-*Benzoin.* Boiling solutions of 1·4 g. of *d*-benzoin-*d*-δ-(α-phenylethyl)semicarbazone in 50 c.c. of absolute alcohol and of 15 g. of oxalic acid in 12 c.c. of water were mixed and boiling was continued for 1 minute. (Longer boiling causes oxidation to benzil derivatives; see J., 1925, **127**, 1282.) The solution, cooled immediately and diluted with 250 c.c. of water, gave a precipitate of *d*-benzoin which was collected after a few hours. Boiling for some time with 200 c.c. of light petroleum (b. p. 60—80°) dissolved the active benzoin but left undissolved the traces of unhydrolysed semicarbazone and other impurities. After cooling and standing, the petroleum extract was filtered and concentrated to half its volume; the *d*-benzoin which crystallised was optically pure after one recrystallisation from absolute alcohol; yield 0·7 g.; m. p. 133—134°; mixed m. p. with synthetic *d*-benzoin (with which it is identical in appearance) 133—134°; $\alpha_D^{11°} + 5·954$, $[\alpha]_D^{11°} + 118·3°$ ($c = 1·2581$ in acetone; $l = 4$).

(2) l-*Benzoin.* 1·6 G. of *l*-benzoin-*l*-δ-(α-phenylethyl)semicarbazone were hydrolysed in an exactly similar fashion. The liberated *l*-benzoin was recrystallised once from light petroleum and once from alcohol, and was then optically pure; yield 0·8 g.; m. p. 133—134°; $\alpha_D^{11°} - 5·435°$, $[\alpha]_D^{11°} - 118·5°$ ($c = 1·1467$ in acetone; $l = 4$). Oxidation of both the active benzoins with nitric acid yielded benzil.

The gummy product referred to on p. 2487 was dissolved in boiling alcohol, then mixed with a hot, concentrated, aqueous solution of oxalic acid, and boiled for 5 minutes. The mixture of solid and semi-solid, obtained after dilution with water and standing, was separated by ether into sparingly soluble (m. p. above 200°), soluble (m. p. 129—132°), and very soluble (a gum) fractions. The first fraction on recrystallisation from alcohol proved to be *benzildi*-d-δ-(*α-phenylethyl*)*semicarbazone*, long, fine needles, m. p. 233° (Found : N, 15·86. $C_{32}H_{32}O_2N_6$ requires N, 15·79%); $\alpha_D^{17°} + 3·08°$, $[\alpha]_D^{17°}$ 178·2° (c = 0·4320 in glacial acetic acid; $l = 4$). By boiling in alcohol with concentrated hydrochloric acid—but not with oxalic acid—it was hydrolysed to benzil. The second fraction on fractional recrystallisation from ether gave chiefly inactive benzoin, which separated first, followed by a crop of benzoin showing lævorotation, m. p. 132—133°; $\alpha_D^{17°} - 0·46°$, $[\alpha]_D^{17°} - 25·7°$ ($c = 0·8974$ in absolute alcohol; $l = 2$). The corresponding gummy product

obtained in the condensation of benzoin and *l*-δ-(α-phenylethyl)semicarbazide hydrochloride gave, on hydrolysis with oxalic acid, a sparingly soluble product (m. p. 238°), *r*-benzoin (m. p. 134°), and benzoin (m. p. 131—133°) showing dextrorotation.

We propose to extend our investigations to the resolution of other racemic ketones and aldehydes by means of active semicarbazides.

We wish to thank the Carnegie Trust for the Universities of Scotland for grants which have partly defrayed the cost of this work.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW. [*Received, June 11th*, 1928.]

CCCXXX.—*The Nitration and Bromination of 4-Methylbenzophenone.*

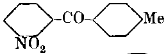
By WILLIAM BLAKEY and HAROLD ARCHIBALD SCARBOROUGH.

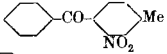
IT has been shown (J., 1927, 2865) that the influence of a methoxyl group, in the 4-position, in the benzophenone series is to direct the first entering substituent into the 3-position; and that further substitution leads to the 3'- and the 5-positions being occupied successively. The halogens, which are usually classed with the methoxyl group since their ortho-para directive power is also to be ascribed to a conjugative effect, behave in the benzophenone series in a different manner, in that the first entering substituent goes into the unsubstituted nucleus (compare Kunckel, *Ber.*, 1904, **37**, 3485; Montagne, *Ber.*, 1916, **49**, 2262). It thus seemed of interest to investigate the behaviour of the methyl group, the least active of the ortho-para directive series, and compare it with that of the methoxyl group and of a halogen.

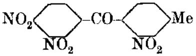
In an investigation of the products of nitration of phenyl-*p*-tolylmethane, Zincke and Milne (*Ber.*, 1872, **5**, 685) showed that a nitroderivative of 4-methylbenzophenone was formed; and in a further communication, Zincke and Plascuda (*Ber.*, 1874, **7**, 983) described the preparation of the mono-, di-, and tri-nitro-derivatives of the ketone, ascribing the structure 3'-nitro-4-methylbenzophenone (I) to the first because it was oxidised by chromic anhydride in glacial acetic acid solution to *m*-nitrobenzoic acid.

A synthesis of 3'-nitro-4-methylbenzophenone, from *m*-nitrobenzoyl chloride and toluene, was carried out by Limpricht and Lenz (*Annalen*, 1895, **286**, 324), but neither this compound nor its derivatives had the properties ascribed to them by Zincke and Plascuda. Basing their opinion upon the product of oxidation,

Limpricht and Lenz reassigned to the alleged substance (I) the structure 2-nitro-4-methylbenzophenone (II): further, they suggested that the continued nitration of 3′-nitro-4-methylbenzophenone yielded 2 : 3′-dinitro-4-methylbenzophenone, and that 3′-nitro-, 4′-nitro-, 2 : 3′-, and 2 : 4′-dinitro-4-methylbenzophenones all gave the same trinitro-compound (III).

(I.) 

 (II.)

 (III.)

The evidence upon which these structures are based seems to be very slender, and, moreover, appears to be contrary to the rules of substitution: the matter was therefore re-investigated.

The nitration of 4-methylbenzophenone, in fuming nitric acid solution, yielded 3-*nitro*-4-*methylbenzophenone*, of which the constitution was established by condensing 3-nitro-*p*-toluoyl chloride with benzene. Under the same conditions, 3′-nitro-4-methylbenzophenone was converted into 3 : 3′-*dinitro*-4-*methylbenzophenone*; the same product was also obtained when 3-nitro-4-methylbenzophenone was nitrated in cold sulphuric acid solution. Further, 4′-nitro-4-methylbenzophenone yielded 3 : 4′-*dinitro*-4-*methylbenzophenone*, since on partial reduction and deamination 3-nitro-4-methylbenzophenone resulted.

The continued nitration of 3 : 3′-dinitro-4-methylbenzophenone in sulphuric acid solution, at 80°, yielded 3 : 3′ : 5-*trinitro*-4-*methylbenzophenone*, which was also obtained when the product of condensation of 3 : 5-dinitro-*p*-toluoyl chloride and benzene was nitrated in sulphuric acid solution, the assigned structure being thus established. Further nitration of 3 : 4′-dinitro-4-methylbenzophenone with a slight excess of nitric acid and in sulphuric acid solution gave 3 : 4′ : 5-*trinitro*-4-*methylbenzophenone*, whereas by use of a large excess of nitric acid at 80°, 3 : 3′ : 4′ : 5-*tetranitro*-4-*methylbenzophenone* was obtained. The proof of the structure of these compounds depends largely upon their reactions with *p*-nitrosodimethylaniline and with piperidine.

The bromination of 4-methylbenzophenone, which was effected by dissolving the compound in a large excess of dry bromine, gave 3-*bromo*-4-*methylbenzophenone*, the structure being established by a synthesis of the compound from 3-bromo-*p*-toluoyl chloride and benzene, and also by reducing 3-nitro-4-methylbenzophenone to the amine and replacing the amino-group by bromine. Under the same conditions 3′- and 4′-nitro- and 3′ : 5′-*dinitro*-4-*methylbenzophenones*

were brominated and in each case the bromine atom entered the 3-position. In the first two cases the products were reduced to the corresponding amino-compounds, and removal of the amino-group yielded 3-bromo-4-methylbenzophenone, thus establishing the constitutions.

The nitration of 4′-chloro-4-methylbenzophenone, in nitric acid solution, gave an almost quantitative yield of *4′-chloro-3-nitro-4-methylbenzophenone*, which was also obtained when 3-nitro-*p*-toluoyl chloride was condensed with chlorobenzene. Further nitration, in sulphuric acid solution, yielded *4′-chloro-3 : 3′-dinitro-4-methylbenzophenone* of which the structure was established by condensing 4-chloro-3-nitrobenzoyl chloride with toluene and nitrating the product by fuming nitric acid. Continued nitration, in sulphuric acid solution at 60°, gave *4′-chloro-3 : 3′ : 5-trinitro-4-methylbenzophenone*; the same compound was obtained on nitration of *4′-chloro-3 : 5-dinitro-4-methylbenzophenone*, which was itself prepared by condensing 3 : 5-dinitro-*p*-toluoyl chloride with chlorobenzene, whereby the structure was established.

On bromination of 4′-chloro-4-methylbenzophenone in excess of dry bromine, *4′-chloro-3-bromo-4-methylbenzophenone* was formed in quantitative yield; its structure was established by reducing 4′-chloro-3-nitro-4-methylbenzophenone to the amine and then replacing the amino-group by bromine.

The results show that the methyl group exerts a marked directive influence, and that the first substituent enters in the ortho-position to this group. The presence of one or two nitro-groups or a chlorine atom in the phenyl nucleus does not appear to affect the position taken np by the entering snbstituent. The second entering substituent goes to the 3′-position, and the presence of a substituent in the 3-position of the tolyl nucleus would appear to inhibit further substitution in this nucleus. The third entering substituent occupies the 5-position whatever the nature of the substitnents previously introduced. The formation of a single product on the further snbstitution of 4′-chloro-4-methylbenzophenone was to be expected from a consideration of the substitution products of 4-chloro- and of 4-methyl-benzophenone.

A comparison between the behaviour of the methyl and the methoxyl groups shows that they are alike in that the sequence in which substituents enter is the same, with one exception, and the methods hy which these substituents are introduced are similar. They differ in that on di- and tri-substitution the methyl group leads to only one isolable isomeride, whereas with the methoxyl group at least two isomerides are obtained.

EXPERIMENTAL.

4-Methylbenzophenone was prepared from benzoyl chloride and toluene according to the method described by Meyer (*Monatsh.*, 1907, **28**, 1223); it separated from light petroleum in plates, m. p. 56°.

3-Nitro-4-methylbenzophenone.—This was obtained (*a*) from 4-methylbenzophenone by dissolving it in nitric acid (*d* 1·5) and allowing the solution to stand for 1 hour, or (*b*) from 3-nitro-*p*-toluic acid by conversion into the acid chloride, with excess of thionyl chloride, and condensation with benzene in the presence of aluminium chloride; it crystallised from acetic acid or from alcohol in faintly yellow plates, m. p. 129° (Found: N, 5·95. $C_{14}H_{11}O_3N$ requires N, 5·8%).

On reduction of this compound with tin and hydrochloric acid, decomposition of the tin double salt with 30% sodium hydroxide solution, and extraction of the free base with ether, *3-amino-4-methylbenzophenone* was obtained; it separated from methyl alcohol in needles, m. p. 109° (Found: N, 6·7. $C_{14}H_{13}ON$ requires N, 6·65%). The *hydrobromide* separated from its solution in dilute acid in long needles, m. p. 130° (Found: HBr, 27·5. $C_{14}H_{13}ON,HBr$ requires HBr, 27·7%); the *acetyl* derivative, formed by refluxing the base for 6 hours with a mixture of acetic acid and acetic anhydride, crystallised from methyl alcohol in needles, m. p. 108° (Found: C, 76·05; H, 5·95. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·95%).

3-Bromo-4-methylbenzophenone.—This was obtained (*a*) when 3-amino-4-methylbenzophenone was diazotised and treated with cuprous bromide; (*b*) when 4-methylbenzophenone was dissolved in dry bromine and the solution allowed to stand in sunlight for 2 days, the excess of bromine being removed in a current of air and by treatment with sulphurous acid; and (*c*) when 3-bromo-*p*-toluic acid was converted into the acid chloride and condensed with benzene in the presence of aluminium chloride. It separated from methyl alcohol in needles, m. p. 107° (Found: Br, 29·1. $C_{14}H_{11}OBr$ requires Br, 29·1%).

3 : 3′-*Dinitro-4-methylbenzophenone.*—5 G. of 3-nitro-4-methylbenzophenone were dissolved in 10 c.c. of sulphuric acid and 5 c.c. of acetic acid, treated with 2 c.c. of nitric acid (*d* 1·5), and the solution allowed to stand for 2 days. A mixture of di- and tri-nitro-derivatives was precipitated on pouring into water, and the more soluble dinitro-compound was isolated by repeated extractions with small quantities of methyl alcohol. The same product, 3 : 3′-*dinitro-4-methylbenzophenone*, was obtained when 3′-nitro-4-methylbenzophenone was dissolved in nitric acid (*d* 1·5) and the solution allowed to stand for 2 hours. It crystallised from methyl alcohol in

faintly yellow plates, m. p. 135° (Limpricht and Lenz, *loc. cit.*, give m. p. 125°) (Found : N, 9·8. $C_{14}H_{10}O_5N_2$ requires N, 9·8%).

3 : 5-*Dinitro-4-methylbenzophenone*.—5 G. of 3 : 5-dinitro-*p*-toluic acid were refluxed with an excess of thionyl chloride, the excess was removed, and the residue dissolved in 100 c.c. of benzene; 10 g. of aluminium chloride were added gradually, and the reaction completed on the water-bath. 3 : 5-*Dinitro-4-methylbenzophenone* crystallised from alcohol in small, yellow plates, m. p. 109° (Found : N, 9·8. $C_{14}H_{10}O_5N_2$ requires N, 9·8%).

5-*Nitro-3-amino-4-methylbenzophenone*, prepared from this compound by reduction with hydrogen sulphide in alcoholic ammonia solution, crystallised from alcohol in deep orange needles, m. p. 157° (Found : N, 11·0. $C_{14}H_{12}O_3N_2$ requires N, 10·95%).

3 : 3′ : 5-*Trinitro-4-methylbenzophenone*.—When 3 : 5-dinitro-4-methylbenzophenone, dissolved in sulphuric acid, was treated with an excess of nitric acid (*d* 1·5) and the solution allowed to stand for some days at room temperature, or when 3-nitro-, 3′-nitro-, or 3 : 3′-dinitro-4-methylbenzophenone was further nitrated under similar conditions, 3 : 3′ : 5-*trinitro-4-methylbenzophenone* was obtained; it separated from acetic acid in pale yellow needles, m. p. 173° (Found : N, 12·55. $C_{14}H_9O_7N_3$ requires N, 12·65%).

3 : 4′-*Dinitro-4-methylbenzophenone*.—This was prepared by dissolving 4′-nitro-4-methylbenzophenone in an excess of nitric acid (*d* 1·5) and allowing the solution to stand for 2 hours; it separated from alcohol in faintly yellow plates, m. p. 130° (compare Limpricht and Lenz, *loc. cit.*).

3-*Nitro-4′-amino-4-methylbenzophenone*.—A warm solution of 10 g. of 3 : 4′-dinitro-4-methylbenzophenone in a mixture of 200 c.c. of alcohol and 10 c.c. of ammonia (*d* 0·880) was treated with hydrogen sulphide until saturated; after removal of a part of the alcohol, the residue was poured into dilute hydrochloric acid, heated, and filtered. An unstable hydrochloride separated on cooling. The free *base* was liberated with ammonia; it crystallised from methyl alcohol in yellow plates, m. p. 164° (Found : N, 11·0. $C_{14}H_{12}O_3N_2$ requires N, 10·95%). On removal of the amino-group in the usual manner, 3-nitro-4-methylbenzophenone (m. p. 129°) was obtained.

3 : 4′ : 5-*Trinitro-4-methylbenzophenone*.—5 G. of 4′-nitro-4-methylbenzophenone, dissolved in 20 c.c. of sulphuric acid, were treated with 4 c.c. of nitric acid (*d* 1·5), the solution was kept for 24 hours, and the reaction completed on the water-bath. The product crystallised from acetic acid in pale yellow needles, m. p. 160° (Found : N, 12·7. $C_{14}H_9O_7N_3$ requires N, 12·65%). This compound did not react with piperidine, but with *p*-nitrosodimethylaniline in alcoholic solution it yielded a light brown, amorphous powder which could not be

obtained in a sufficiently pure state for analysis. When the trinitro-compound was reduced with hydrogen sulphide in alcoholic ammonia solution, and the product worked up in the manner previously described, *3-nitro-4′ : 5-diamino-4-methylbenzophenone* was obtained; it separated from dilute acetone in orange plates, m. p. 202° (Found: N, 15·2. $C_{14}H_{13}O_3N_3$ requires N, 15·5%). 3-Nitro-4-methylbenzophenone was obtained on the removal of the amino-groups, thus suggesting that one of these groups was present in each nucleus.

3 : 3′ : 4′ : 5 - *Tetranitro - 4 - methylbenzophenone*.—When either 3 : 4′-dinitro- or 3 : 4′ : 5-trinitro-4-methylbenzophenone was dissolved in a mixture of equal volumes of sulphuric and nitric acids and heated on the water-bath for 6 hours, 3 : 3′ : 4′ : *5-tetranitro-4-methylbenzophenone* was obtained; it separated from acetic acid in small, yellow prisms, m. p. 187° (Found: N, 14·9. $C_{14}H_8O_9N_4$ requires N, 14·9%). This compound reacted with piperidine, with boiling alcoholic ammonia, and with sodium methoxide, but in each case the product was a brown powder which could not be recrystallised from any of the usual solvents.

3 - *Bromo* - 3′ - *nitro* - 4 - *methylbenzophenone* was obtained when 3′-nitro-4-methylbenzophenone was treated with an excess of dry bromine; it separated from alcohol in faintly yellow plates, m. p. 124° (Found: Br, 24·85. $C_{14}H_{10}O_3NBr$ requires Br, 25·0%). On reduction with stannous chloride in alcoholic hydrogen chloride solution, *3-bromo-3′-amino-4-methylbenzophenone* was obtained, which crystallised from dilute methyl alcohol in yellow needles, m. p. 94° (Found: Br, 27·6. $C_{14}H_{12}ONBr$ requires Br, 27·6%); deamination yielded 3-bromo-4-methylbenzophenone (m. p. 107°).

3′ : *5′-Dinitro-4-methylbenzophenone*, prepared by condensation of 3 : 5-dinitrobenzoyl chloride with toluene in the presence of aluminium chloride, crystallised from methyl alcohol in faintly yellow plates, m. p. 134° (Found: N, 9·8. $C_{14}H_{10}O_5N_2$ requires N, 9·8%); on treatment with an excess of dry bromine, this yielded *3-bromo-3′ : 5′-dinitro-4-methylbenzophenone*, which separated from alcohol or acetic acid in faintly yellow needles, m. p. 173° (Found: N, 7·7. $C_{14}H_9O_5N_2Br$ requires N, 7·65%). The structure of the latter compound follows from its analogy with 3-bromo-3′-nitro-4-methylbenzopbenone.

3-Bromo-4′-nitro-4-methylbenzophenone, prepared from 4′-nitro-4-methylbenzophenone in the manner previously described, crystallised from alcohol in faintly yellow plates, m. p. 119° (Found: Br, 24·85. $C_{14}H_{10}O_3NBr$ requires Br, 25·0%); on reduction with stannous chloride in alcoholic hydrogen chloride solution, *3-bromo-4′-*

amino-4-methylbenzophenone was formed: faintly yellow needles, m. p. 162°, from methyl alcohol (Found: N, 5·0. $C_{14}H_{12}ONBr$ requires N, 4·9%). Deamination yielded 3-bromo-4-methylbenzophenone (m. p. 107°).

4′-Chloro-3-nitro-4-methylbenzophenone, obtained when *p*-chlorobenzoyl chloride was condensed with toluene in the presence of aluminium chloride, and the product (m. p. 128°) dissolved in excess of nitric acid (*d* 1·5) and allowed to stand for 12 hours, separated from methyl alcohol in long needles, m. p. 98°. It was also obtained when 3-nitro-4′-amino-4-methylbenzophenone was diazotised and treated with cuprous chloride (Found: N, 5·15. $C_{14}H_{10}O_3NCl$ requires N, 5·1%). Reduction of this nitro-compound in the usual manner gave *4′-chloro-3-amino-4-methylbenzophenone*, which crystallised from methyl alcohol in faintly yellow prisms, m. p. 142° (Found: N, 5·6. $C_{14}H_{12}ONCl$ requires N, 5·7%).

4′-Chloro-3′-nitro-4-methylbenzophenone was prepared by dissolving 4-chloro-3-nitrobenzoyl chloride in toluene in the presence of aluminium chloride; it separated from methyl alcohol in heavy yellow prisms, m. p. 121° (Found: N, 5·2; Cl, 12·85. $C_{14}H_{10}O_3NCl$ requires N, 5·1; Cl, 12·9%).

4′-Chloro-3 : 3′-dinitro-4-methylbenzophenone was obtained when the foregoing compound was dissolved in nitric acid (*d* 1·5) and the solution allowed to stand for 24 hours; or when 4′-chloro-3-nitro-4-methylbenzophenone, dissolved in sulphuric acid, was treated with a slight excess of nitric acid. In the latter case, the product was a mixture of di- and tri-nitro-compounds. The substance crystallised from methyl alcohol or dilute acetone in yellow prisms, m. p. 131° (Found: N, 8·75. $C_{14}H_9O_5N_2Cl$ requires N, 8·75%).

4′-Chloro-3 : 5-dinitro-4-methylbenzophenone, resulting from the condensation of 3 : 5-dinitro-4-toluoyl chloride and chlorobenzene in presence of aluminium chloride, crystallised from alcohol or acetic acid in yellow plates, m. p. 118° (Found: N, 8·8. $C_{14}H_9O_5N_2Cl$ requires N, 8·75%).

4′-Chloro-3 : 3′ : 5-trinitro-4-methylbenzophenone was obtained when 3′-nitro- or 3 : 3′- or 3 : 5-dinitro-4′-chloro-4-methylbenzophenone was dissolved in a mixture of sulphuric and nitric acids and the solution gently warmed or allowed to stand for some days at the ordinary temperature; it separated from acetic acid in heavy, yellow needles, m. p. 182° (Found: N, 11·45. $C_{14}H_8O_7N_3Cl$ requires N, 11·5%).

4′-Chloro-3-bromo-4-methylbenzophenone was prepared by dissolving 4′-chloro-4-methylbenzophenone in dry bromine, and by treating a diazotised solution of 4′-chloro-3-amino-4-methylbenzo-

phenone with cuprous bromide; it crystallised from alcohol in needles, m. p. 122° (0·1756 G. gave 0·1885 g. of silver halides $C_{14}H_{10}OClBr$ requires 0·1880 g.).

THE UNIVERSITY CHEMICAL LABORATORIES,
CAMBRIDGE. [*Received, July 4th*, 1928.]

CCCXXXI.—*The Constituents of Some Indian Essential Oils. Part XXV. l-α- and l-β-Curcumenes.*

By B. SANJIVA RAO and JOHN LIONEL SIMONSEN.

RAO, SHINTRE, and SIMONSEN (*J. Ind. Inst. Sci.*, 1926, **9A**, 140) separated from the essential oil occurring in the rhizomes of *Curcuma aromatica*, Salisb., a sesquiterpene to which they gave the name *l*-curcumene. The hydrocarbon, characterised by the preparation of a number of crystalline derivatives, appeared to be homogeneous and to be monocyclic with three ethylenic linkages. Since it was obtainable comparatively readily in quantity, we decided to attempt to determine its constitution, a problem which it seemed all the more desirable to elucidate, since only a few monocyclic sesquiterpenes have been studied, bisabolene and zingiberene being the more important.

Early in the investigation, evidence was obtained that *l*-curcumene, in spite of its apparent homogeneity, was a mixture of at least two hydrocarbons, the crystalline nitrosate and trihydrochloride previously described being derived from two different sesquiterpenes. It was observed that the yields of these two derivatives varied very considerably with different specimens of the oil, and further, when the sesquiterpene fraction was warmed with dilute sulphuric acid or treated with sodium in amyl-alcoholic solution, the recovered hydrocarbon gave the nitrosate in undiminished yield but the crystalline trihydrochloride could no longer be obtained. Fractional distillation of the oil, from which the trihydrochloride had been separated, showed the presence of a sesquiterpene monohydrochloride, the parent hydrocarbon of which (see p. 2501) gave the crystalline nitrosate in a yield exceeding that obtained with the original terpene, whilst treatment with hydrogen chloride did not give any trihydrochloride. The presence of at least two hydrocarbons in the sesquiterpene "*l*-curcumene" having thus been proved, it became necessary to devise methods for the preparation of each of them in a pure state prior to undertaking experiments on their constitution. In this we have been successful, and as it is no longer possible for us to collaborate, we have decided to place on record the results so far obtained.

We have designated the hydrocarbon yielding the crystalline .itrosate and the liquid monohydrochloride l-*α-curcumene*. This ubstance can be obtained fairly pure by treatment of the mono-ydrochloride with sodium acetate in acetic acid solution, but it is btained in a much higher state of purity by a somewhat indirect iethod. Treatment of the nitrosate with alcoholic potassium ydroxide solution yields l-*oximino-α-curcumene*, $C_{15}H_{22}$:NOH, a olourless oil which can be distilled in small quantities without ecomposition. It was characterised by the preparation of a rystalline *benzoyl* derivative, m. p. 84—85°, and a *monohydro-hloride*, m. p. 135—136°. The latter substance is not a salt, but is ›rmed by the addition of hydrogen chloride to one of the ethylenic nkages, since it is not decomposed by alkali. So far as we are ware, this is the first oximino-derivative obtained directly from a esquiterpene. Semmler and Bode (*Ber.*, 1907, **40**, 1129) and emmler and Hoffmann (*ibid.*, p. 3527) have described the oximes of -santalal, an aldehyde obtained by the oxidation of a primary lcohol present in sandal-wood oil, and of cedrone, a ketone formed y the oxidation of cedrene. We have not succeeded in converting ie above-mentioned oxime into the parent ketone (or aldehyde), ut further experiments in this direction are contemplated, for little ppears to be known of the properties of the sesquiterpene ketones.

When *l*-oximino-α-curcumene is reduced with sodium in ethyl-coholic solution it is converted into l-*dihydro-α-curcumenylamine*, $_{15}H_{25}$·NH_2, one of the ethylenic linkages having been reduced as ell as the oximino-group. The base, which was most readily ırified through its sparingly soluble *hydrogen oxalate*, was a viscid l possessing a strong ammoniacal smell. The reduction of one of ie ethylenic linkages on passing from the oximino-derivative to the ıse was not anticipated and was somewhat unfortunate, since it had ›en hoped to introduce a fourth ethylenic linkage by submitting ie base to a Hofmann degradation process. It was then expected ıat, by molecular rearrangement, a substituted derivative of ›nzene would have resulted which might have proved suitable for ıidation experiments. This reaction would open up a new method attacking the problem of the constitution of the sesquiterpenes. is proposed to study the properties of the sesquiterpene amines, ıly two other members of the series having been previously scribed (Semmler and Hoffmann, *loc. cit.*; Semmler and Mayer, ›r., 1911, **44**, 3678).

Methylation of *l*-dihydro-α-curcumenylamine with methyl iodide the presence of alkali yields l-*dihydro-α-curcumenyltrimethyl-mmonium iodide*, $C_{15}H_{25}$·NMe_3I, which crystallises well and gives e corresponding hydroxide on treatment with silver oxide. This

substance, which was also obtained crystalline, could not be purified since it was extremely hygroscopic, but when distilled unde diminished pressure, it decomposed smoothly with formation o a mixture of a hydrocarbon and a base. The base was an oi distilling without decomposition, and analysis showed it to b l-*dimethyldihydro-α-curcumenylamine*, $C_{15}H_{25}\cdot NMe_2$. It did not yiel any crystalline derivatives.

The hydrocarbon was the main product of the degradatio and was found to be very pure *l*-α-curcumene. The yield of nitrosat from the terpene prepared in this manner was very much higher tha from that regenerated from the monohydrochloride (see p. 2501 On treatment with hydrogen chloride in acetic acid solution, it giv a quantitative yield of a monohydrochloride. *l*-α-Curcumene is ve stable. It is not reduced by sodium when dissolved in either eth or amyl alcohol, nor is it attacked by dilute sulphuric acid. I alkaline solution it is only slowly oxidised by potassium perma ganate, whilst titration with bromine in chloroform solution sho the presence of only one ethylenic linkage. The physical properti of the hydrocarbon indicate, however, that it is monocyclic and must therefore contain three ethylenic linkages. Two of these a remarkably inert, and this is not without analogy (compare Ruzic and co-workers, *Helv. Chim. Acta,* 1922, **5**, 331; 1923, **6**, 67 1924, **7**, 1875; *Rec. trav. chim.*, 1928, **47**, 363). When *l*-α-curcume is reduced catalytically with hydrogen in the presence of platin oxide (Adams and Shriner, *J. Amer. Chem. Soc.*, 1923, **45**, 217 addition of six hydrogen atoms takes place with formation of t saturated hydrocarbon, *hexahydro-α-curcumene*, $C_{15}H_{30}$, which optically inactive.

Whilst this reaction appears to confirm the presence of th ethylenic linkages, it cannot be regarded as conclusive, since it l been shown (Iyer and Simonsen, J., 1926, 2049) that a *cyclo*propa ring can be reduced catalytically. It was therefore decided examine the action of benzoylhydroperoxide on the terpene, si it has been shown by Nametkin (*J. pr. Chem.*, 1926, **112**, 1 1927, **115**, 56) and Meerwein (*ibid.*, 1926, **113**, 56) that this reag is especially suitable for the estimation of ethylenic linkages. T experiments (see p. 2505) establish definitely the presence of th such linkages in *l*-α-curcumene.

It has not been found possible to dehydrogenate the sesquiterp with either sulphur or selenium with formation of a naphthal derivative, as Ruzicka, Meyer, and Mingazzini (*Helv. Chim. A* 1922, **5**, 345) succeeded in doing in the case of the monocy sesquiterpene, zingiberene. This would appear to indicate t *l*-α-curcumene does not contain a " potential " naphthalene nucl

·-β-Curcumene has been regenerated in a pure state from its ıydrochloride by treatment with anhydrous sodium acetate in :tic acid solution. It is a monocyclic terpene containing three ylenic linkages, the presence of which can be proved readily by :ation with bromine as well as by the formation of the trihydro-oride. On catalytic reduction l-*hexahydro*-β-*curcumene* is formed, reduction proceeding much more readily than in the case of the meride, and the product was optically active. We are not in a sition to say whether the two fully reduced hydrocarbons are ncturally identical. Oxidation with benzoylhydroperoxide also ıceeded smoothly and confirmed the presence of three ethylenic ‹ages.

Jnlike the α-hydrocarbon, *l*-β-curcumene is very unstable and ·eadily isomerised. After treatment of the hydrocarbon with % sulphuric acid or with sodium in amyl-alcoholic solution, crystalline trihydrochloride can no longer be isolated, although reduction takes place in the latter reaction. It seems probable m the properties of the recovered hydrocarbon that the action dilute sulphuric acid results in the formation of a dicyclic pene, and this will be further investigated. Dehydrogenation h either sulphur or selenium did not lead to any recognisable ducts.

Reference has been made above to the fact that *l*-dihydro-ırcumenylamine belongs to a type of base which has been little died, and it therefore appeared of interest to have its physio-cal properties examined. Dr. T. A. Henry kindly arranged for base to be tested by Dr. J. Trevan at the Wellcome Physiological search Laboratories, and we are very much indebted to him for following report :

(1) On the pithed cat (brain destroyed) : 0·4 mg. as hydro-pride, no effect ; 4·0 mg., a very slight rise in blood pressure ; ng. caused a fall in blood pressure from heart failure.

(2) On isolated rabbit's uterus in Ringer's solution, a concen-:ion of 1/5000 of the hydrochloride killed the muscle.

(3) In an etherised cat with intact brain, 4 mg. produced a ht fall in blood pressure.

The base has therefore no characteristic physiological action ond a general toxic action."

n its toxic properties this base thus resembles the unsaturated ne obtained by the reduction of santonin oxime (Fränkel, " Die zneimittel-Synthese," p. 737) and the unsaturated dicyclic ne, camphenamine (*op. cit.*, p. 743).

EXPERIMENTAL.

The sesquiterpene used in these experiments was separated as described in the previous communication (*loc. cit.*, p. 143). It was carefully purified by distillation over sodium and had b. p. 127—129°/6 mm. The constants of the oil obtained in different preparations varied somewhat ($d_{30°}^{30°}$ 0·8760—0·8764; $n_D^{30°}$ 1·4929—1·4940; $[\alpha]_D^{30°}$ − 19·4° to − 25·9°; $[R_L]_D$ 67·67—67·74). This somewhat large variation was due to the different proportions of *l*-α- and *l*-β-curcumenes present in the oil, as indicated by a similar variation in the respective yields of nitrosate and trihydrochloride obtained. Since *l*-β-curcumene is readily isomerised, it appeared possible that distillation over sodium might be injurious, but this was found not to be the case. A specimen of the original sesquiterpene was purified by repeated distillation without the use of sodium, and the constants were very similar (b. p. 129—130°/7 mm.; $d_{30°}^{30°}$ 0·8790; $n_D^{30°}$ 1·4944; $[\alpha]_D^{30°}$ −20·8°). The relative yields of nitrosate and trihydrochloride were not affected by distillation over sodium. An attempt was made to separate *l*-α- and *l*-β-curcumene by fractional distillation through a four-pear Young still-head; ten fractions, b. p. 129—131°/7 mm., were taken, but the difference in physical properties was small [(1) $d_{30°}^{30°}$ 0·882; $n_D^{30°}$ 1·4932; $[\alpha]_D^{30°}$ −22·0°; (5) $d_{30°}^{30°}$ 0·881; $n_D^{30°}$ 1·4940; $[\alpha]_D^{30°}$ −24·8°; (10) $d_{30°}^{30°}$ 0·8740; $n_D^{30°}$ 1·4940; $[\alpha]_D^{30°}$ −24·1°]. No difference was observed in the yields of nitrosate and of trihydrochloride from the ten different fractions of the hydrocarbon.

l-α-*Curcumene.*

Nitrosate.—To a well-cooled mixture of *l*-curcumene (10 c.c.), amyl nitrite (8 c.c.), and acetic acid (20 c.c.), nitric acid (*d* 1·42; 8 c.c.) was gradually added, efficient stirring being essential during the addition; the mixture was kept for some hours, then alcohol was added, and the voluminous precipitate collected and well washed with alcohol. As previously found (*loc. cit.*, p. 143), the nitrosate after crystallisation from methyl alcohol had m. p. 100—101°, but a sample which was recrystallised after 3 weeks' keeping had m. p. 110° (compare Earl and Kenner, J., 1927, 1275). The nitrosate is readily soluble in most of the ordinary organic solvents with the exception of methyl and ethyl alcohols and light petroleum. In chloroform solution (c = 5·634) $[\alpha]_D^{30°}$ −20·4°. A chloroform solution of the nitrosate did not decolorise bromine and was not acted upon by hydrogen chloride in ethereal solution. The yield of the nitrosate varied considerably (2·3—4·5 g. from 10 g.), depending upon the sample of *l*-curcumene used in its preparation.

l-α-Curcumenenitrolbenzylamine.—A mixture of the nitrosate (5 g.), benzylamine (3·6 g.), and alcohol (20 c.c.) was heated on the water-bath for 1 hour. On cooling and addition of water, an oil separated which slowly crystallised. It separated from dilute alcohol in leaflets, m. p. 102—104°. In methyl alcohol ($c = 2·46$) $[\alpha]_D^{30°}$ −19·5° (Found : N, 8·5. $C_{22}H_{32}ON_2$ requires N, 8·2%).

l-α-Curcumene Monohydrochloride.—A well-cooled solution of *l*-curcumene (10 g.) in acetic acid (30 c.c.) was saturated with hydrogen chloride, and after standing over-night the mixture was poured on ice. The partly crystalline oil was dissolved in ether, the ether dried and evaporated, and the residue cooled in a freezing mixture. The solid, *l*-β-curcumene trihydrochloride, was removed by filtration through an ice-cooled funnel, and when the liquid hydrochlorides were fractionated under diminished pressure, *l-α-curcumene monohydrochloride* was readily obtained pure, b. p. 150—155°/8 mm. (Found : Cl, 14·7. $C_{15}H_{25}Cl$ requires Cl, 14·8%). The hydrochloride is a colourless oil which has no tendency to crystallise. As was the case with the nitrosate, the relative yields of trihydrochloride and monohydrochloride showed very considerable variation.

In an experiment made with the object of regenerating the parent hydrocarbon, a mixture of the monohydrochloride (40 g.), acetic acid (100 c.c.), and anhydrous sodium acetate (50 g.) was heated in a bath at 140° for 2½ hours. The hydrocarbon separated by distillation in steam and fractionation over sodium had b. p. 118—120°/5 mm.; $d_{30°}^{30°}$ 0·8690, $n_D^{30°}$ 1·4926, $[\alpha]_D^{30°}$ −22·1°; when it was titrated with bromine in chloroform solution, 1 mol. of bromine was absorbed, and treatment with hydrogen chloride did not yield any crystalline trihydrochloride, indicating the absence of *l*-β-curcumene. The hydrocarbon did not, however, consist of pure *l*-α-curcumene, since the yield of nitrosate was low (2 g. from 10 g.).

l-Oximino-α-curcumene.—When *l*-α-curcumene nitrosate in acetic acid was treated with zinc dust, a vigorous reaction ensued which was difficult to control, and a mixture of hydrocarbons and alcohols was formed. The following method was adopted as the most convenient for the preparation of the oximino-derivative.

The freshly prepared nitrosate was dissolved in the minimum quantity of hot alcohol and heated on the water-bath with an equivalent amount of alcoholic potassium hydroxide for 20 minutes. An excess of water was added, the oil which separated extracted with ether, the ether dried, and evaporated. *l-Oximino-α-curcumene* is best purified by distillation under diminished pressure, but it is necessary to distil only small quantities at a time to avoid decomposition. It is thus obtained as a colourless, viscid oil, b. p. 182—

185°/7 mm., $d_{30^\circ}^{30^\circ}$ 0·9817; $n_D^{30^\circ}$ 1·5134; $[\alpha]_D^{30^\circ}$ − 27·2°; $[R_L]_D$ 71·37 (Found: C, 77·5; H, 9·6. $C_{15}H_{23}ON$ requires C, 77·2; H, 9·9%). On titration with bromine in chloroform solution, the presence of only one ethylenic linkage was indicated, although the molecular refraction agrees fairly closely with the value (72·07) required for three such linkages. The oxime is insoluble in aqueous potassium hydroxide and in both aqueous and alcoholic solutions of hydrochloric acid; it is, however, soluble in alcoholic potassium hydroxide. Attempts to prepare a crystalline acetyl derivative or oximino-oxime were unsuccessful.

The *benzoyl* derivative, prepared by the Schotten–Baumann reaction, was only obtained crystalline with difficulty and could not be recrystallised, m. p. 84—85° (Found: N, 4·7. $C_{22}H_{27}ON$ requires N, 4·4%). The *monohydrochloride* was formed when an ethereal solution of the oxime was saturated with hydrogen chloride. It crystallised from alcohol in plates, m. p. 135—136° (Found: Cl, 12·9. $C_{15}H_{24}ONCl$ requires Cl, 13·2%). The hydrochloride was very stable and was not acted upon by cold alkali.

l-*Dihydro-α-curcumenylamine*.—To a boiling solution of *l*-oximino-α-curcumene (10 g.) in ethyl alcohol (120 c.c.), sodium (15 g.) was added as rapidly as possible. When all the sodium had dissolved, the base was distilled in steam, dissolved in ether, and the ethereal extract repeatedly washed with dilute hydrochloric acid (1 : 1). The well-cooled solution of the hydrochloride was basified with sodium hydroxide solution and the resulting oil (5 g.) isolated by extraction with ether. The crude base was mixed with an excess of an aqueous solution of oxalic acid, and the sparingly soluble *hydrogen oxalate* which separated was collected; when crystallised from water it separated in clusters of fine needles, m. p. 143—144°, containing 1 mol. of water of crystallisation, which was lost at 100°. It was readily soluble in methyl alcohol, acetone, and benzene, but very sparingly soluble in cold water, ethyl acetate, and chloroform. A chloroform solution of the oxalate was stable to bromine (Found: C, 62·2; H, 9·3; N, 4·1; H_2O, 5·3. $C_{17}H_{29}O_4N,H_2O$ requires C, 62·0; H, 9·4; N, 4·3; H_2O, 5·5%).

l-*Dihydro-α-curcumenylamine*, obtained by the decomposition of the pure oxalate, is a colourless, viscid oil with a strong basic smell, b. p. 151—152°/17 mm.; $d_{30^\circ}^{30^\circ}$ 0·9026; $n_D^{30^\circ}$ 1·4983; $[\alpha]_D^{30^\circ}$ − 22·2°; $[R_L]_D$ 71·85. The molecular refraction agrees closely with the value (71·76) required for two ethylenic linkages (Found: C, 81·6; H, 11·9; N, 6·5. $C_{15}H_{27}N$ requires C, 81·4; H, 12·2; N, 6·3%). Crystalline derivatives of the base could not be obtained with hydrochloric, perchloric, tartaric, or picric acid; the sulphate was a solid, but was not obtained pure. The base can also be

prepared by the reduction of *l*-α-curcumenylamine nitrosate with sodium and alcohol, and this is probably the most convenient method for its preparation in quantity.

The *acetyl* derivative was formed when a mixture of the base (3 g.) and acetic anhydride (1·4 g.) was allowed to remain in a desiccator over sulphuric acid for 24 hours. The crystalline solid which separated was purified from light petroleum and obtained in needles, m. p. 109—110° (Found: C, 77·9; H, 10·7; N, 5·5. $C_{17}H_{29}ON$ requires C, 77·6; H, 11·0; N, 5·3%).

l-*Dihydro-α-curcumenyltrimethylammonium Iodide and Hydroxide.*—The trimethylammonium iodide is obtained in a poor yield when the base in either methyl-alcoholic or acetone solution is treated with methyl iodide. For its preparation in quantity the following method was adopted: The base (1 mol.) was suspended in aqueous sodium hydroxide solution (1 : 2; 5 mols.), and to the hot solution methyl iodide (4—5 mols.) was added drop by drop, the reaction being complete in 4—5 hours. After the reaction mixture had stood for 2 days, the greater portion of the iodide had separated as a crystalline solid. A further quantity can be obtained by saturating the alkaline solution with carbon dioxide, evaporating it to dryness under diminished pressure, and extracting the inorganic salts with alcohol. The crude iodide was best purified by solution in water, saturation of the solution with carbon dioxide, and evaporation to dryness under diminished pressure. The dry residue was dissolved in alcohol and filtered from inorganic salts, and after removal of the alcohol the residue was finally recrystallised from ether, the *trimethylammonium iodide* being obtained in needles, m. p. 163—164° (Found: C, 55·5; H, 8·9; I, 2·8. $C_{18}H_{34}NI$ requires C, 55·2; H, 8·7; I, 3·2%).

For the preparation of the hydroxide, the iodide was shaken in aqueous solution with an excess of freshly prepared silver oxide for several hours. The filtered, strongly alkaline solution was concentrated under diminisbed pressure at the ordinary temperature, and finally dried over phosphoric oxide, a crystalline solid being ohtained. The hydroxide was extremely hygroscopic and became pasty immediately on exposure to the atmosphere. It was not found possible to purify and analyse it.

l-*α-Curcumene and* l-*Dimethyldihydro-α-curcumenylamine.*—The hydroxide (10 g.) was distilled under diminished pressure (400 mm.), the distillate being collected in dilute sulphuric acid. After separation of the insoluble oil (A) by ether, the acid solution was basified with dilute sodium hydroxide solution, and the organic base extracted with ether. On removal of the solvent, an oil (2 g.) remained, b. p. 130—140°/15 mm.; $d_{30°}^{30°}$ 0·8824; $n_D^{30°}$ 1·4913;

$[\alpha]_D^{30°}$ −23·0° (Found : C, 82·0; H, 12·2; N, 5·6. $C_{17}H_{31}N$ requires C, 81·9; H, 12·4; N, 5·9%). l-*Dimethyldihydro-α-curcumenylamine* was a viscid oil with a strong basic smell; it did not yield any crystalline derivatives.

The oil (A) was distilled over sodium, b. p. 128—130°/7 mm. $d_{30°}^{30°}$ 0·8633; $n_D^{30°}$ 1·4944; $[\alpha]_D^{30°}$ −22·9°; $[R_L]_D$ 68·23. It was identified as very pure l-α-*curcumene*. It was only very slowly attacked by potassium permanganate in alkaline solution, and when dissolved in chloroform it absorbed one mol. of bromine. Treatment with hydrogen chloride in acetic acid solution gave a quantitative yield of the monohydrochloride (Found : Cl, 14·6. Calc. : Cl, 14·8%) and no trace of a trihydrochloride. The yield of nitrosate was very much higher than that obtained from any other sample of the hydrocarbon examined (0·45 g. from 0·8 g. of the hydrocarbon). *l*-α-Curcumene was not reduced by sodium in ethyl-alcoholic solution, the physical constants of the recovered oil being unchanged, nor was it isomerised by heating at 380° in an inert atmosphere. It did not yield a naphthalene derivative when heated at 270° with sulphur or selenium. A solution in acetic acid gives, with a drop of sulphuric acid, a yellow coloration gradually changing to pink.

Hexahydro-α-curcumene.—A mixture of *l*-α-curcumene (10 c.c.), acetic acid (40 c.c.), and platinum oxide (0·3 g.) (Adams and Shriner, *loc. cit.*) was shaken with hydrogen at a pressure of 2 atm. Reduction was complete after 50 hours and it was necessary to revive the catalyst twice by treatment with oxygen. The *hexahydro-α-curcumene* was a viscid, colourless oil, b. p. about 128°/7 mm. $d_{30°}^{30°}$ 0·8283; $n_D^{30°}$ 1·4592; $[\alpha]_D^{30°}$ + 0°; $[R_L]_D$ 69·36 (Calc., 69·27) (Found : C, 86·0; H, 14·0. $C_{15}H_{30}$ requires C, 85·7; H, 14·2%). It did not absorb bromine in chloroform solution.

l-β-*Curcumene*.

A mixture of the trihydrochloride (see p. 2501) (80 g.), acetic acid (300 c.c.), and anhydrous sodium acetate (110 g.) was heated at 140° for 8 hours. After addition of water, the sesquiterpene was distilled in steam, dried, and purified by repeated distillation over sodium. l-β-*Curcumene* is a thick, colourless oil, b. p. 128—130°/6 mm. $d_{30°}^{30°}$ 0·8810; $n_D^{30°}$ 1·4940; $[\alpha]_D^{30°}$ −27·9°. The hydrocarbon did not yield a crystalline nitrosate, and on treatment with hydrogen chloride the trihydrochloride (m. p. 84—85°) was regenerated in a yield of more than 50% of the theoretical. Titration with bromine in chloroform solution gave figures agreeing closely with those required for the presence of three ethylenic linkages, whilst in the presence of alkali a solution of potassium permanganate was im

iediately decolorised. An acetic acid solution gives with a drop of ilphuric acid a deep brown coloration.

When the hydrocarbon was heated on the water-bath for some ours with a dilute solution of sulphuric acid (10%), it was converted ito what would appear to be a dicyclic terpene, b. p. 115—117°/7 im.; $d_{30°}^{30°}$ 0·8932; $n_D^{30°}$ 1·4936; $[\alpha]_D^{30°}$ − 11·9°; $[R_L]_D$ 66·43. This ew hydrocarbon, which awaits investigation, does not yield any ystalline derivatives. *l*-β-Curcumene is not reduced by sodium i amyl-alcoholic solution, but undergoes isomerisation and no longer ields the characteristic trihydrochloride (b. p. 129—130°/7 mm.; $_{30°}^{30°}$ 0·8780; $n_D^{30°}$ 1·4936). Isomerisation was also observed when ie terpene was heated in an inert atmosphere at 380° under pressure. Io naphthalene derivatives were formed when the terpene was eated at 270° with either sulphur or selenium.

l-β-*Hexahydrocurcumene.*—*l*-β-Curcumene was catalytically hydro-enated under the same conditions as were used for *l*-α-cur-umene. The hydrogenation proceeded with greater ease and was omplete in 10 hours. The saturated hydrocarbon had b. p. about 28°/7 mm.; $d_{30°}^{30°}$ 0·8283; $n_D^{30°}$ 1·4552; $[\alpha]_D^{30°}$ + 6·3° (Found: C, 5·9; H, 14·2. $C_{15}H_{30}$ requires C, 85·7; H, 14·2%).

Oxidation of l-α- *and* l-β-*Curcumenes with Benzoylhydroperoxide.*—Veighed quantities of each of the sesquiterpenes were mixed with n excess of a standard solution of benzoylhydroperoxide (von 'echmann and Vanino, *Ber.*, 1894, **27**, 1511; Levy and Legrange, *Bull. Soc. chim.*, 1925, **37**, 1597) in chloroform solution, and main-ained at 10—15° until oxidation was complete. A portion of the olution was removed from time to time for titration against sodium hiosulphate in the presence of potassium iodide. Oxidation was ound to be complete after about 478 hours, during which period solution of benzoylhydroperoxide in chloroform kept under imilar conditions showed no appreciable alteration in strength. 'he results confirmed the presence of three ethylenic linkages in each ydrocarbon (*l*-α-Curcumene: peroxide used corresponded to 133·2 c.c. of $Na_2S_2O_3$ solution; calc., 137·3 c.c. *l*-β-Curcumene: per-xide used corresponded to 140·4 c.c. of $Na_2S_2O_3$ solution; calc., 33·6 c.c.).

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CCCXXXII.—*Equilibrium in the Systems* $ZnSO_4$–Na_2SO_4–H_2O *at* 0° *and* 25° ; $MnSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 35° ; *and* $CoSO_4$–K_2SO_4–H_2O *at* 25°.

By Robert Martin Caven and William Johnston.

Koppel and Gumperz (*Z. physikal. Chem.*, 1905, **52**, 409) have investigated the double salts formed by sodium sulphate with a series of the sulphates of the bivalent metals. These double sulphates are formed, not at 0°, but at higher temperatures. However, while Koppel and Gumperz were mainly interested in the double salts formed, the present authors are more concerned with the type of isotherms given by the various systems. Thus, whilst Koppel (*Z. physikal. Chem.*, 1903, **42**, 1) showed that the double salt $CuSO_4,Na_2SO_4,2H_2O$ does not crystallise below 16·7° from a solution of its component salts, the authors (J., 1927, 2358) investigated the isotherms of the system $CuSO_4$–Na_2SO_4–H_2O at 0°, 25°, and 37·5°.

Koppel and Gumperz (*loc. cit.*) have shown that the double salt $ZnSO_4,Na_2SO_4,4H_2O$ is formed from a solution of its component salts only above 8·7°. They did not, however, examine the system completely at any given temperature, so it was decided to investigate the isotherms at 0° and 25°.

Geiger (Thesis, Berlin, 1904) alleged that the double salt of manganese sulphate and sodium sulphate existed in two hydrated forms : $MnSO_4,Na_2SO_4,4H_2O$ and $MnSO_4,Na_2SO_4,2H_2O$. According to Marignac (*Ann. Min.*, 1856, **9**, 22), the dihydrate of manganese sodium sulphate crystallises from a solution not below 36·5°, and a tetrahydrate by free evaporation at the ordinary temperature these results were accepted by Koppel (*loc. cit.*).

Schreinemakers and Provije (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 326) investigated the system $MnSO_4$–Na_2SO_4–H_2O at 35°, and noted the formation of two double salts ($9MnSO_4,10Na_2SO_4$ and $MnSO_4,3Na_2SO_4$) according to the composition of the mother-liquor. It was therefore decided to investigate this system at this temperature as well as at 0° and 25°.

The system $CoSO_4$–K_2SO_4–H_2O has been investigated at 25° in order to compare it with the systems $NiSO_4$–K_2SO_4–H_2O (Caven and Johnston, J., 1926, 2628) and $CuSO_4$–K_2SO_4–H_2O (Caven and Mitchell, J., 1924, **125**, 1428) at the same temperature.

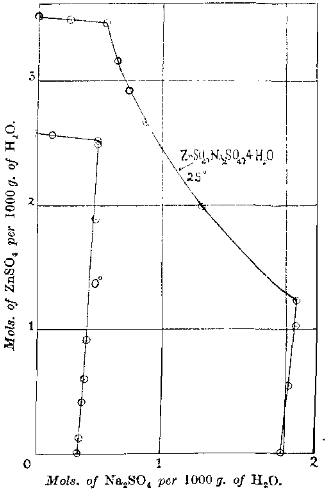
Experimental.

The System $ZnSO_4$–Na_2SO_4–H_2O *at* 0° *and* 25°.—For the investigation at 0°, saturated solutions of the two salts were made at

mospheric temperature, and various proportions of these solutions re placed successively in a flask fitted with a stirrer and kept mersed in ice and water; the mixtures were stirred for 3 days fore portions of the solutions were separated and analysed. For e system at 25°, saturated solutions of the two salts were made at °, and solutions as above placed in a flask immersed in a thermostat 25° ± 0·01°. Zinc was determined by means of standard potassium

FIG. 1.

System $ZnSO_4$–Na_2SO_4–H_2O *at* 0° *and* 25°.



rocyanide solution, and sodium sulphate was calculated after termination of total sulphate.

The results are expressed as mols. per 1000 g. of water, and are own by means of rectangular co-ordinates (Fig. 1).

The System $MnSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 35°.—For this tem at 0°, saturated solutions of the two salts were made at room aperature, and the same procedure as above was carried out. A ghtly different procedure was necessary at 25°. The solubility

TABLE I.

The System $ZnSO_4$–Na_2SO_4–H_2O at 0° and 25°.

(Z = Zinc sulphate; N = Sodium sulphate; D = Double salt.)

Temperature 0°.			Temperature 25°.		
Mols. of $ZnSO_4$ per 1000 g. of H_2O.	Mols. of Na_2SO_4 per 1000 g. of H_2O.	Solid phase.	Mols. of $ZnSO_4$ per 1000 g. of H_2O.	Mols. of Na_2SO_4 per 1000 g. of H_2O.	Solid phase.
—	0·331	N.	—	1·972	N.
0·128	0·347	N.	0·543	2·023	N.
0·414	0·366	N.	1·073	2·084	N.
0·600	0·381	N.	1·226	2·087	N. & D.
0·914	0·388	N.	1·987	1·322	D.
1·886	0·463	N.	2·669	0·871	D.
2·494	0·485	N.	2·922	0·745	D.
2·521	0·492	N. & Z.	3·157	0·641	D.
2·568	0·122	Z.	3·463	0·551	D. & Z.
2·589	—	Z.	3·504	0·255	Z.
			3·518	—	Z.

of manganese sulphate decreases above 27°, and there was therefore no advantage in preparing solutions above this temperature. Consequently, solutions of sodium sulphate saturated at 40° and of manganese sulphate saturated at 25° were used. To ensure the presence of a solid phase on the manganese sulphate portion of the isotherm, solid tetrahydrated manganese sulphate (the hydrate stable at 25°) was added to different mixtures of the above solutions. These mixtures were placed in a flask as above, immersed in a thermostat at 25 ± 0·01°, and stirred for 4 days, after which it was found that equilibrium had been reached. At the sodium sulphate end of the isotherm, different proportions of the above solutions were taken, and the mixtures stirred for 3 days. Both solid and liquid phases were analysed. For the experiment at 35°, various proportions of solutions of the two salts saturated at 40° were used, whilst to ensure the presence of the appropriate solid phase, anhydrous sodium sulphate was added at the sodium end of the isotherm and monohydrated manganese sulphate at the manganese end. These mixtures were stirred for 4 days. Both solid and liquid phases were analysed, manganese being estimated volumetrically by the Volhard method, and sodium sulphate calculated after determination of total sulphate.

The results are expressed as mols. per 1000 g. of water (Fig. 2). The results at 25° and 35° are also expressed as g. per 100 g. of solution, and plotted on the triangular diagram in order to show the composition of the double salt (Figs. 3 and 4).

The double salt obtained by us at 25° from an equimolecular solution of its constituent salts was washed with water at the same

temperature, air-dried, and analysed (Found: $MnSO_4$, 45·77; Na_2SO_4, 43·15; H_2O, 11·08. Calc. for $MnSO_4,Na_2SO_4,2H_2O$: $MnSO_4$, 45·88; Na_2SO_4, 43·18; H_2O, 10·94%).

FIG. 2.

System $MnSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 35°.

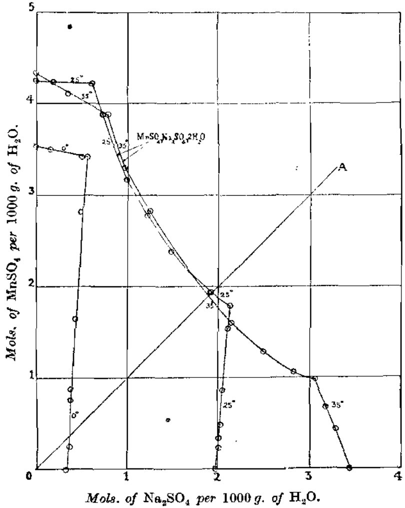


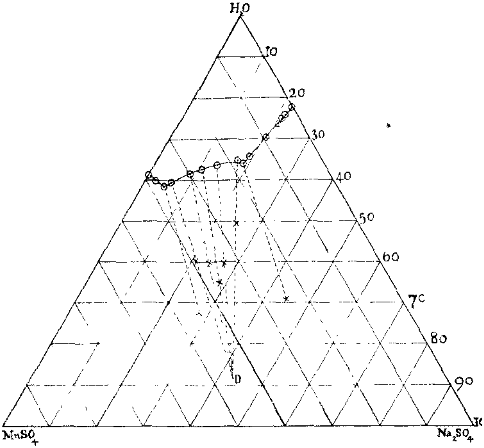
TABLE II.

The System $MnSO_4$–Na_2SO_4–H_2O at 0°.

(M = Manganese sulphate; N = Sodium sulphate.)

Mols. of $MnSO_4$ per 1000 g. of H_2O.	Mols. of Na_2SO_4 per 1000 g. of H_2O.	Solid phase.	Mols. of $MnSO_4$ per 1000 g. of H_2O.	Mols. of Na_2SO_4 per 1000 g. of H_2O.	Solid phase.
—	0·331	N.	2·818	0·520	N.
0·254	0·369	N.	3·413	0·566	N. & M.
0·773	0·389	N.	3·424	0·509	M.
0·897	0·383	N.	3·499	0·158	M.
1·650	0·445	N.	3·533	—	M.

Fig. 3.



Equilibrium diagram for the system $MnSO_4$–Na_2SO_4–H_2O *at* 25°.

The composition of the double salt is shown by the co-ordinates of the po D, at which broken lines drawn through the moist residues intersect, to $MnSO_4,Na_2SO_4,2H_2O$.

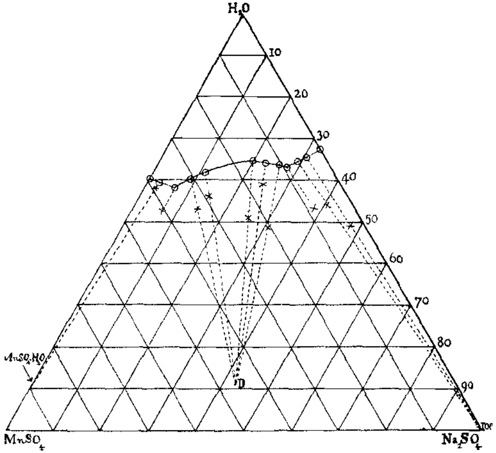
TABLE III.

The System $MnSO_4$–Na_2SO_4–H_2O at 25° and 35°.

(M = Manganese sulphate; N = Sodium sulphate; D = Double salt.)

Temperature 25°.			Temperature 35°.		
Mols. of $MnSO_4$ per 1000 g. of H_2O.	Mols. of Na_2SO_4 per 1000 g. of H_2O.	Solid phase.	Mols. of $MnSO_4$ per 1000 g. of H_2O.	Mols. of Na_2SO_4 per 1000 g. of H_2O.	Solic phase
—	1·972	N.	—	3·440	N.
0·246	2·004	N.	0·431	3·288	N.
0·349	2·003	N.	0·674	3·175	N.
0·491	2·029	N.	0·980	3·063	N. & [illegible]
0·861	2·054	N.	1·055	2·830	D.
1·536	2·108	N.	1·287	2·504	D.
1·786	2·132	N. & D.	1·602	2·144	D.
1·928	1·917	D.	2·821	1·256	D.
2·381	1·494	D.	3·299	0·978	D.
2·767	1·232	D.	3·875	0·790	D. & [illegible]
3·169	1·001	D.	4·109	0·359	M.
3·889	0·742	D.	4·334	—	M.
4·220	0·618	D. & M.			
4·248	0·195	M.			
[illegible]		[illegible]			

FIG. 4.



Equilibrium diagram for the system $MnSO_4$–Na_2SO_4–H_2O *at* 35°.

The composition of the double salt is shown by the co-ordinates of the point), *at which broken lines drawn through the moist residues intersect, to be* $nSO_4,Na_2SO_4,2H_2O$.

TABLE IV.

The System $MnSO_4$–Na_2SO_4–H_2O at 25°.

(D.S. = $MnSO_4,Na_2SO_4,2H_2O$.)

Solutions.			Moist solids.			
$MnSO_4$.	Na_2SO_4.	H_2O.	$MnSO_4$.	Na_2SO_4.	H_2O.	Solid phase.
—	21·89	78·11	—	—	—	$Na_2SO_4,10H_2O$.
2·81	21·54	75·65	—	—	—	
3·94	21·28	74·78	—	—	—	
5·44	21·16	73·40	—	—	—	
9·14	20·53	70·33	—	—	—	
15·15	19·55	65·30	—	—	—	
17·15	19·26	63·59	24·50	44·95	30·55	$Na_2SO_4,10H_2O$ & D.S.
18·62	17·42	63·96	26·26	24·64	49·10	D.S.
22·88	13·51	63·61	33·24	26·87	39·89	
26·23	11·00	62·77	37·26	28·81	33·93	
29·52	8·78	61·70	36·58	23·97	39·45	
34·69	6·23	59·08	39·20	20·94	39·86	
36·94	5·09	57·97	45·01	28·10	26·89	D.S. & $MnSO_4,4H_2O$.
38·43	1·66	59·91	—	—	—	$MnSO_4,4H_2O$.
39·10	—	60·90	—	—	—	

TABLE V.

The System $MnSO_4$–Na_2SO_4–H_2O at 35°.

(*D.S. = $MnSO_4,Na_2SO_4,2H_2O$.*)

Solutions.			Moist solids.			
$MnSO_4$.	Na_2SO_4.	H_2O.	$MnSO_4$.	Na_2SO_4.	H_2O.	Solid phase.
—	32·83	67·17	—	—	—	Na_2SO_4.
4·25	30·49	65·26	3·26	47·92	48·82	Na_2SO_4.
6·55	29·05	64·40	5·45	40·51	54·04	Na_2SO_4.
9·35	27·49	63·16	8·41	38·47	53·12	Na_2SO_4 & D.S.
10·21	25·75	64·04	20·43	31·06	48·51	D.S.
12·54	22·96	64·50	15·62	24·90	59·48	D.S.
15·64	19·70	64·66	23·09	25·78	51·13	D.S.
26·56	11·12	62·32	28·87	15·31	55·82	D.S.
30·43	8·49	61·08	32·65	13·93	53·42	D.S.
34·46	6·62	58·92	45·73	6·65	47·62	D.S. & $MnSO_4,H_2O$.
37·12	3·05	59·83	39·60	3·01	57·39	$MnSO_4,H_2O$.
39·56	—	60·44	—	—	—	$MnSO_4,H_2O$.

The System $CoSO_4$–K_2SO_4–H_2O *at* 25°.—For this system at 25 saturated solutions of the two salts were made at 40°, and variou proportions placed in a flask fitted with a stirrer, and immersed in thermostat at 25° ± 0·01°. The mixtures were stirred for 3 day and liquid phases only analysed. Cobalt was estimated by precip tation as ammonium phosphate, and ignition to pyrophosphat Potassium sulphate was calculated after determination of tot sulphate.

The results are expressed as mols. per 1000 g. of water (Fig. 5).

TABLE VI.

The System $CoSO_4$–K_2SO_4–H_2O at 25°.

(C = Cobalt sulphate; K = Potassium sulphate; D = Double salt.)

Mols. of $CoSO_4$ per 1000 g. of H_2O.	Mols. of K_2SO_4 per 1000 g. of H_2O.	Solid phase.	Mols. of $CoSO_4$ per 1000 g. of H_2O.	Mols. of K_2SO_4 per 1000 g. of H_2O.	Solid phase.
—	0·680	K.	1·372	0·321	D.
0·150	0·737	K.	2·205	0·240	D.
0·239	0·780	K. & D.	2·557	0·212	D. & C
0·458	0·531	D.	2·536	0·190	C.
0·950	0·388	D.	2·433	—	C.
1·095	0·361	D.			

Conclusions.

The Zinc–Sodium System (Fig. 1).—1. No double salt is formed 0°. This is in agreement with the work of Koppel and Gumpe The isotherm simply shows the influence of each salt on the solubili of the other.

2. The double salt $ZnSO_4,Na_2SO_4,4H_2O$ is formed over a co siderable range at 25°.

3. At both 0° and 25°, the solubility of sodium sulphate is increased by addition of zinc sulphate.

4. At both 0° and 25°, the solubility of zinc sulphate is decreased by addition of sodium sulphate. This is in contrast to the system $CuSO_4$–Na_2SO_4–H_2O (Caven and Johnston, *loc. cit.*) where both at 0° and 25° the solubility of copper sulphate is increased by addition of sodium sulphate.

The Manganese–Sodium System (Fig. 2).—1. No double salt is formed at 0°.

2. The double salt $MnSO_4,Na_2SO_4,2H_2O$ (Fig. 3) is the stable salt at 25°, and is formed over a considerable range.

3. $MnSO_4,Na_2SO_4,2H_2O$ (Fig. 4) is also formed at 35° over a wider range. No evidence was found of the formation of the double salts $MnSO_4,3Na_2SO_4$ and $9MnSO_4,10Na_2SO_4$ (Schreinemakers and Provije, *loc. cit.*), or of $MnSO_4,Na_2SO_4,4H_2O$.

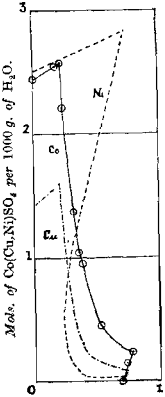
4. A study of the isotherms at 25° and 35° (Fig. 2) shows the interesting fact that the double-salt portion of the 25°-isotherm is nearly coincident along all its length with the double-salt portion of the 35°-isotherm. This indicates that the solubilities of the double salt at these two temperatures are almost identical. A closer inspection of the place where the equimolecular line 0A (Fig. 2) cuts the isotherms shows that the solubility of the double salt $MnSO_4,Na_2SO_4,2H_2O$ is slightly less at 35° than at 25°.

5. *At all three temperatures the solubility of manganese sulphate is decreased* by addition of sodium sulphate. This fact is of much greater interest on more particular examination, for the solid phases are different at the different temperatures. The decrease is least at 25° where the solid phase is $MnSO_4,4H_2O$, and is greatest, being much accentuated, at 35° where the solid phase is $MnSO_4,H_2O$. An intermediate decrease is shown at 0°, where the solid phase is $MnSO_4,7H_2O$. Thus these isotherms show the effect of addition of sodium sulphate on the solubilities of the hepta-, tetra-, and mono-hydrated forms of manganese sulphate.

6. The solubility of $MnSO_4,H_2O$ at 35° is slightly greater than that of $MnSO_4,4H_2O$ at 25°.

FIG. 5.

System Co(Cu,Ni)SO_4–K_2SO_4–H_2O *at* 25°.



Mols. of K_2SO_4 *per* 1000 *g. of* H_2O.

7. At 0° and 25° the solubility of sodium sulphate is increased by addition of manganese sulphate. At 35° it is much decreased by increasing quantities of manganese sulphate. Here again there is a change of solid phase from the decahydrated to the anhydrous state.

The Cobalt–Potassium System (Fig. 5).—1. The double salt $CoSO_4,K_2SO_4,6H_2O$ is formed over a wide range at 25°.

2. The solubility of each single salt is increased by addition of the other.

3. The isotherm is of the general type obtainable for double salts of the form $M^{II}SO_4,M^{I}_2SO_4,6H_2O$. It closely resembles the isotherm for the system $CuSO_4$–K_2SO_4–H_2O at 25° (Caven and Mitchell, *loc. cit.*), but differs considerably from the corresponding isotherm for the system $NiSO_4$–K_2SO_4–H_2O (Caven and Johnston, J., 1926, 2628), which deviates appreciably from the typical isotherm (see Fig. 5).

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ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, July 28th*, 1928.]

CCCXXXIII.—*The Chemistry of the Three-carbon System. Part XIX. The Homomesitones.*

By AILEEN EDITH ABBOTT, GEORGE ARMAND ROBERT KON, and RALPH DAVID SATCHELL.

IN searching for readily accessible examples of neutral tautomeric substances, we were led to examine the ketones $C_8H_{14}O$, derived from the intermolecular condensation of methyl ethyl ketone, to which the name homomesitones was applied by Porlezza and Gatti (*Gazzetta*, 1925, **25**, 224). Theoretically, there are four possible homomesitones if the very unlikely formation of the substance $CH_2Me{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}COMe$ be left out of consideration.

(I.)	$CH_2Me{\cdot}CMe{:}CH{\cdot}COEt$	$CHMe{:}CMe{\cdot}CH_2{\cdot}COEt$	(II.)
(III.)	$CH_2Me{\cdot}CMe{:}CMe{\cdot}COMe$	$CHMe{:}CMe{\cdot}CHMe{\cdot}COMe$	(IV.)

These two pairs of compounds are related to one another in the same way as the ketones studied by Kon and Linstead (J., 1925, **127**, 815) and should exhibit tautomerism of the same general character. Homomesitones have been obtained by a variety of methods, but little was known of their chemistry until Bodroux and Taboury (*Bull. Soc. chim.*, 1908, **3**, 831; 1909, **5**, 950), who obtained their product with the aid of calcium carbide, attempted to characterise it by means of the very indefinite semicarbazone melting at 119—120°; subsequently, Becker and Thorpe (J., 1922,

121, 1303) obtained the same ketone and concluded that it had the structure (I) because it condensed with ethyl sodiomalonate to a *dihydroresorcinol* which gave *β-methyl-β-ethylglutaric acid* on oxidation; a similar conclusion was reached by Ekeley and Howe (*J. Amer. Chem. Soc.*, 1923, **45**, 1917), who prepared their ketone with the aid of both alkaline and acid condensing agents.

The experience accumulated in the last few years suggested that the ketone (II) would probably be encountered together with (I) in the crude homomesitone prepared in the presence of sodium ethoxide, whilst the mobility of the three-carbon system present in these compounds would doubtless enable (II) to condense with ethyl sodiomalonate just as readily as (I). Closer investigation brought to light considerable divergences in the properties of homomesitones from different sources, and it was therefore necessary to characterise the different compounds met with. The task proved to be one of great difficulty owing to the extremely intractable nature of the mixtures of ketones obtained from methyl ethyl ketone, more especially with the aid of alkaline condensing agents. The semicarbazones prepared from these mixtures are extremely soluble in the crude state, have but little tendency to crystallise, and are probably mixtures of stereoisomerides. For this reason *it is only possible to isolate a very small proportion of the constituents* of a given mixture in the pure state. We ultimately succeeded in establishing the mutual relationships between the different homomesitones by recourse to synthesis, and the results can be briefly summarised as follows: (*a*) Alkaline condensing agents lead to mixtures of (I) and (II), the former predominating especially in the ketone obtained by Bodroux and Taboury's method; the *ketone* (I) forms a characteristic *semicarbazone*, m. p. 162°. (*b*) Acid condensing agents lead to ketones with a branched chain (III or IV), sulphuric acid giving a ketone of low density, consisting mainly of the βγ-compound (IV), whereas hydrochloric acid yields a ketone of high density and refractive index, consisting mainly of (III); by far the best method is that of Descudé (*Ann. Chim. Phys.*, 1903, **29**, 486), which generally gives (III) only. The formation of ketones with a branched chain is not altogether unexpected, because it has been shown by Harries and his pupils that aromatic aldehydes condense with methyl ethyl and methyl propyl ketones to give compounds such as CHPh:CR·COMe in presence of hydrochloric acid, whilst straight-chain compounds are formed in alkaline solution. It is surprising that Ekeley and Howe did not suspect differences of structure in the homomesitones prepared by them and subsequently used for synthetic purposes.

The structure of the homomesitones (I), (III), and (IV) was

confirmed by synthesis from the corresponding acids which were prepared by standard methods; all attempts to synthesise the compound (II), however, were unsuccessful, and the only way in which this substance could be obtained consisted in treating the equilibrium mixture of (I) and (II) with aluminium amalgam which converts (I) into a bimolecular reduction product, leaving the $\beta\gamma$-ketone unattacked.

There are definite indications that the homomesitones are capable of *cis-trans* isomerism; thus, the ketone (IV) gives two *semicarbazones*, m. p. 203—204° and 163°, although mixtures melting at about 175° are usually encountered. The *semicarbazone* of (III) has a form of m. p. 166—167° in addition to the usual one, m. p. 186°. The ketone obtained by the action of magnesium ethyl iodide on ethyl ethoxycrotonate (Blaise and Maire, *Ann. Chim. Phys.*, 1908, **15**, 566), which forms a semicarbazone (m. p. 158°) *not* identical with that of (I), must be a stereoisomeride of the latter; stereoisomerism in this case cannot be due to the existence of two forms of the semicarbazone, because the regenerated ketone yields the same semicarbazone on recombining with semicarbazide (compare Locquin and Heilmann, *Compt. rend.*, 1928, **186**, 705). In addition to this, every unsymmetrical ketone can theoretically give rise to two semicarbazones, and it may be that the homomesitones (I) and (II) do actually yield mixtures of *cis-trans* isomeric derivatives, which would in part account for the nature of the semicarbazone usually obtained from them.

Tautomerism of the Homomesitones.—Investigation proves that the homomesitones exhibit tautomerism of the nature to be expected from their structure. In presence of sodium ethoxide or methoxide they form equilibrium mixtures similar to those recently studied by Dickins, Hugh, and Kon (this vol., p. 1630). It is a remarkable fact, however, that both as regards mobility and point of equilibrium the two pairs of homomesitones are very different. Thus, the ketones (I) and (II) form an equilibrium mixture containing 67·5% of the $\alpha\beta$-compound, and this mixture is, as might be expected, indistinguishable from the crude homomesitone obtained by the action of sodium ethoxide on methyl ethyl ketone. The mobility of the system is high, equilibrium being practically established in 24 hours at room temperature. The ketones (III) and (IV) in presence of sodium ethoxide form an equilibrium mixture containing only 17% of the $\alpha\beta$-compound, and the mobility is so low that the equilibration of the $\alpha\beta$-ketone only proceeded half-way in the course of a fortnight at room temperature. The final equilibrium had to be determined at the boiling point of the reagent, and was only reached after 9 hours.

The difference between the two pairs of ketones must evidently be attributed to the effect of the α-methyl group present in (III) and (IV) which has already been found to favour the βγ-phase in some cases (Kon and Narayanan, J., 1927, 1536), although no such effect was observed in the acids studied by Goldberg and Linstead (this vol., p. 2349). The great effect on mobility is certainly unexpected, and further work will be necessary before any explanation is attempted; it is therefore proposed to study several suitable cases in the near future.

EXPERIMENTAL.

Action of Acid Condensing Agents on Methyl Ethyl Ketone.

1. *Sulphuric Acid.*—Ice-cold methyl ethyl ketone was treated with one-tenth of its volume of sulphuric acid, the mixture kept for 24 hours, and worked up as described by Ekeley and Howe (*loc. cit.*). The yield of homomesitones was poor, generally about 10%, b. p. mainly 60—62°/17—19 mm., together with a fraction, b. p. 65—70°. The first fraction, $d_{4^{\circ}}^{20\cdot3^{\circ}}$ 0·85845, $n_{D}^{20\cdot3^{\circ}}$ 1·44552, was readily converted into a crystalline semicarbazone; this was fractionally crystallised from methyl alcohol, the less soluble portion being obtained in long, transparent laminæ, m. p. about 175°; on repeated crystallisation from ethyl alcohol, the m. p. rose to 203—204°, the compound being identical with the *semicarbazone* of (IV) (see below) (Found: N, 23·3. $C_9H_{17}ON_3$ requires N, 22·9%). The more soluble constituent of the original mixture was obtained in plates, m. p. 134°, evidently consisting of a "eutectic" similar to those previously obtained (compare Kon and Linstead, *loc. cit.*).

The fraction, b. p. 65—70°/17 mm., gave a semicarbazone from which iridescent, anthracene-like plates, m. p. 186°, were obtained on fractional crystallisation from methyl alcohol; these were identical with the semicarbazone of (III) (see below).

A somewhat better yield of homomesitones could be obtained by increasing the amount of condensing agent used; thus from 500 c.c. of methyl ethyl ketone and 200 c.c. of acid in four portions, 82 g., b. p. 53—85°/14 mm., were obtained, from which similar products were isolated.

2. *Hydrochloric Acid.*—The condensation was carried out as described by Ekeley and Howe; in later experiments, the mixture was kept for only 8 days. A yield of some 40% of homomesitone fraction was obtained, boiling mainly above 65°/20 mm.; the principal fraction, b. p. 65—67°/19 mm., had $d_{4^{\circ}}^{20\cdot4^{\circ}}$ 0·8689, $n_{D}^{20\cdot4^{\circ}}$ 1·45133. The same semicarbazone was obtained from all the fractions; it was purified by grinding with light petroleum, and fractionally crystallised from methyl alcohol. The first crops

usually melted at about 172° and had the characteristic anthracene like appearance of the αβ-compound, m. p. 186°; repeated fractional crystallisation from methyl alcohol or acetone raised the m. p. to about 180°, whilst a compound of identical appearance, m. p. 166—167°, was present in the more soluble fraction and was evidently a stereoisomeride. Both semicarbazones gave rise to similar ketones: (*a*), from the high-melting semicarbazone, b. p. 53°/13 mm., $d_4^{18.8°}$ 0·86722, $n_D^{18.8°}$ 1·45313, $[R_L]_D$ 39·32; (*b*), from the low-melting semicarbazone, b. p. 53°/13 mm., $d_4^{19.6°}$ 0·86567, $n_D^{19.6°}$ 1·45233, $[R_L]_D$ 39·32; the same semicarbazones were obtainable from these ketones, although the higher-melting compound was clearly not quite homogeneous. This fact and the difficulty in eliminating all traces of halogen from the product caused us to abandon the use of hydrochloric acid as a condensing agent.

3. *Descudé's Method.*—The first experiment according to Descudé's directions (*loc. cit.*) gave a somewhat poor yield of homomesitone which was an inseparable mixture of αβ- and βγ-ketones (III and IV). The following simplified process gave good results: 300 G. of methyl ethyl ketone and 300 g. of acetyl chloride were cooled below 0°, and 120 g. of powdered zinc chloride added, the mixture being kept in the ice-chest for 2 days. Water and a little ether were added, and the oil was washed with sodium carbonate and added to a hot solution of 100 g. potassium hydroxide in 100 c.c. of water and 300 c.c. of alcohol, the mixture being boiled under reflux for 5 minutes. Water was then added, the oil extracted by ether, thoroughly washed, dried, and fractionated with a good column. The fractions obtained were: (*a*) up to 50°/20 mm., 30 g.; (*b*) 50—55°/18 mm., 9 g.; (*c*) 55—58°/17 mm., 22 g.; (*d*) 58—63°/16 mm., 27 g.; (*e*) 63—73°/15 mm., 38 g. Fractions (*b*), (*c*), and (*d*) were converted into the *semicarbazone* which formed characteristic plates, m. p. 186° after one crystallisation, and was identical with the synthetic specimen (see below) (Found: C, 59·0; H, 9·4. $C_9H_{17}ON_3$ requires C, 59·0; H, 9·4%). The ketone regenerated from it with oxalic acid had b. p. 53°/10 mm., 160°/750 mm., $d_4^{19.5°}$ 0·86957, $n_D^{19.5°}$ 1·45293, $[R_L]_D$ 39·19; it had a strong, pleasant odour. The fraction (*a*) consisted of methyl ethyl ketone and some of the βγ-ketone which could be isolated in the form of its semicarbazone. The fraction (*e*) still contained chlorine and was therefore again treated with alkali, whereby a mixture of the two homomesitones was obtained, the αβ- predominating. A greater proportion of the βγ-ketone was obtained on more prolonged treatment with alkali; thus, after 3 hours' boiling with sodium ethoxide in excess, it became the main product.

Synthesis of Ketone (III).—Methyl ethyl ketone was condensed

with ethyl α-bromopropionate in the presence of zinc to *ethyl β-hydroxy-αβ-dimethyl-*n*-valerate*, b. p. 89—90°/13 mm., $d_4^{19.5°}$ 0·96457, $n_D^{19.5°}$ 1·4319 (75% yield). The acid obtained by alkaline hydrolysis was liquid. It was dehydrated by boiling with acetic anhydride and gave a poor yield of *αβ-dimethyl-Δ^α-pentenoic acid*, b. p. 116°/18 mm., $d_4^{17.5°}$ 0·97497, $n_D^{17.5°}$ 1·45952, $[R_L]_D$ 36·06 (calc., 35·60). The *acid chloride* boiled at 66°/17 mm., and gave a p-*toluidide* forming long needles, m. p. 123° (Found: C, 77·3; H, 8·7. $C_{14}H_{19}ON$ requires C, 77·4; H, 8·8%). The acid chloride was treated with zinc methyl iodide (compare Dickins, Hugh, and Kon, *loc. cit.*), giving a moderate yield of ketone which was converted into the semicarbazone and the latter recrystallised from methyl alcohol. The first crop separated in characteristic anthracene-like crystals, m. p. 180—182°, identical with the semicarbazone prepared by the Descudé method. Subsequent crops melted much lower and were evidently impure. The ketone, *γδ-dimethyl-Δ^γ-hexen-β-one* (III), regenerated from the first crop of semicarbazone had b. p. 65°/20 mm., $d_4^{17.4°}$ 0·86856, $n_D^{17.4°}$ 1·45283, $[R_L]_D$ 39·23, and was in every way identical with that obtained by Descudé's method.

Synthesis of Ketone (IV).—Ethyl β-hydroxy-αβ-dimethyl-*n*-valerate was readily dehydrated with phosphorus oxychloride in benzene, giving a 95% yield of *ethyl αβ-dimethyl-Δ^β-pentenoate*, b. p. 69°/13 mm., $d_4^{21.1°}$ 0·92379, $n_D^{21.1°}$ 1·43628. The *acid*, obtained by allowing the ester (1 g.-mol.) to stand at room temperature with 70 g. of sodium hydroxide in 700 c.c. of aqueous alcohol for 3 days (compare Linstead and May, J., 1927, 2565), had b. p. 116°/20 mm., $d_4^{18.2°}$ 0·97002, $n_D^{18.2°}$ 1·4498, $[R_L]_D$ 35·50 (calc., 35·60). The *acid chloride* boiled at 52°/13 mm., and gave a p-*toluidide* which had little tendency to crystalliso but formed needles, m. p. 56°, from dilute alcohol (Found: C, 77·5; H, 8·7. $C_{14}H_{19}ON$ requires C, 77·4; H, 8·8%). The acid chloride gave on treatment with zinc methyl iodide a 50—60% yield of ketone, but an 85% yield was more readily obtained by slowly adding magnesium methyl iodide to a well-cooled ethereal solution of the acid chloride. The ketone was isolated in the form of its sparingly soluble semicarbazone; this separated very rapidly, and after one crystallisation melted at about 175°, rising to 203—204° after repeated crystallisation. The regenerated ketone, *γδ-dimethyl-Δ^δ-hexen-β-one* (IV), had a characteristic camphoraceous odour, b. p. 48°/12 mm., 154°/750 mm., $d_4^{19.2°}$ 0·85385, $n_D^{19.2°}$ 1·43768, $[R_L]_D$ 38·74 (calc., 38·72). It was found that another *semicarbazone* was generally present and sometimes constituted the sole product; this had a very similar appearance (long, flattened needles) but melted at 163°, and the ketone regenerated from it was indistinguishable from the above,

b. p. 45°/10 mm., $d_4^{16\cdot9°}$ 0·85601, $n_D^{16\cdot9°}$ 1·4401, but gave the low-melting semicarbazone on treatment with semicarbazide. This ketone was frequently obtained as the main product on treating the intermediate fractions of the "Descudé ketone" with hot sodium ethoxide.

Equilibrium between Ketones (III) and (IV).—For the analysis of mixtures of the two ketones, the method of Linstead and May (*loc. cit.*) was used. The values obtained in 10 minutes with *M*/300-solutions in chloroform were

Mixture (% αβ)	0	10	25	50	75	90	100
% Iodine addition	81·8	77·7	69·6	50·6	28·4	14·5	3·4

from which a reference curve was constructed.

1. *Point of equilibrium.* Equilibrium was only slowly established at room temperature. Samples of the two pure ketones were therefore treated with a slight excess of sodium in methyl alcohol (4% solution) and warmed on the steam-bath under reflux for 6 hours; the ketones were then isolated as described by Dickins, Hugh, and Kon (*loc. cit.*), analysed iodometrically, and again treated with the reagent.

Initial material :	αβ-Ketone.			βγ-Ketone.	
Time (hours)	6	12	18	6	12
% Iodine addition	58·9	73·5	73·8	74·5	74·3
% αβ-Ketone	40·0	18·25	17·25	16·5	16·75

The equilibrium point is therefore 17 ± 0·25%.

2. *Mobility.* The first experiments were carried out by adding a cold solution of sodium (4 g.) in 75 c.c. of methyl alcohol to 18·3 g. of the ketone, making the volume up to 100 c.c. with methyl alcohol, and keeping the mixture at room temperature, 20 c.c. of solution being withdrawn at intervals for analysis.

Initial material :	αβ-Ketone.						
Time (hours)	24	48	72	96·5	121	235	422
% Iodine addition	11·7	16·6	18·4	22·4	27·0	37·9	46·2
% αβ-Ketone	92·5	87·5	85·5	81·05	76·5	64·75	55·5

Initial material :	βγ-Ketone.		
Time (hours)	96	165	306
% Iodine addition	79·5	78·9	78·1
% αβ-Ketone	5·75	6·75	9·0

The values for 235 and 422 hours were obtained by combining the five fractions of ketone isolated, taking them as corresponding to 72 hours, and again treating them with sodium methoxide. Only a few experiments were performed with the βγ-ketone, because this was apt to give erratic results. Finally, in order to obtain an estimate of mobility comparable with that of the ketones (I) and

) (see below), the αβ-ketone was treated with N-sodium methide (1 equiv.) at 25° :

ne (hours)	24	48	72
Iodine addition	14·6	17·2	20·9
αβ-Ketone	89·5	86·5	82·5

e change thus proceeded somewhat more quickly at 25°, although total concentration of the reactants was lower.

Action of Alkaline Condensing Agents on Methyl Ethyl Ketone.

1. *Calcium Carbide.*—The condensation was carried out essentially described by Bodroux and Taboury (*loc. cit.*); the yield of homo-sitone fraction varied, the best being about 55%. On redistil-ion, the bulk of the product boiled at 67—70°/20 mm. and had $^{8°}$ 0·85523, $n_{D}^{22·8°}$ 1·44973, $[R_L]_D$ 39·57; these properties indicate high percentage of αβ-ketone, but this varies in different prepar-ons. The semicarbazone was prepared in the usual way and oved to be an extremely intractable material from which only a nute proportion of pure substances could be isolated. Washing th light petroleum and fractional crystallisation from methyl cohol led to the isolation of a very small amount of a less soluble nstituent (in addition to the completely insoluble disemicar-zone already obtained by Ekeley and Howe, *loc. cit.*). This parated in pearly plates, m. p. 162°, and was the *semicarbazone* the ketone (I) (see below) (Found : N, 23·1. $C_9H_{17}ON_3$ requires 22·9%). From the more soluble portions, less definite solids varying m. p. were obtained, mainly the " eutectic " melting 123°; this gave a ketone very similar in properties to the pure -ketone, *viz.*, b. p. 50—52°/9 mm., $d_{4°}^{18·8°}$ 0·85731, $n_{D}^{18·8°}$ 1·45193, $_L]_D$ 39·64. On one occasion a very small amount of needles, m. p. 6°, was isolated, which depressed the m. p.'s of all the other pure micarbazones, but the amount was insufficient for investigation. another occasion a preparation, m. p. 137°, was isolated which peared to be a definite compound, and the ketone regenerated m it had b. p. 52—53°/12 mm., $d_{4°}^{19·8°}$ 0·85777, $n_{D}^{19·8°}$ 1·45163, $_L]_D$ 39·63. On recombination with semicarbazide, a mixture was tained from which a small amount of the compound of m. p. 2° could be isolated.

2. *Sodium Ethoxide.*—The following simplified preparation gave tisfactory results : Sodium (60 g.) was dissolved in ethyl alcohol 0 c.c.) and the excess of alcohol evaporated off under reduced essure at about 80°; to the mixture, cooled in ice and salt, 500 c.c. methyl ethyl ketone were added and the whole was kept for hours with occasional shaking. Water was then added, the taken up in ether, well washed, dried, and distilled, the yield

of homomesitone fraction (b. p. 62—70°/19 mm.) being 90—100 g The main bulk had $d_4^{21.4°}$ 0·85656, $n_D^{21.4°}$ 1·44502, iodine addition 34·3%. A specimen of the ketone prepared by the carbide process gave, on treatment with excess of sodium ethoxide, a product of very similar properties and iodine addition, which are characteristic of the equilibrium mixture of αβ- and βγ-ketone.

The semicarbazone of this equilibrium mixture was prepared, but it was again found impossible to isolate more than a small amount of pure material from it, although the αβ-semicarbazone, m.p. 162°, was obtained without great difficulty.

Synthesis of the Ketone (I).—β-Methyl-β-ethylacrylic acid was prepared as described by Kon and Linstead (J., 1925, **127**, 616) or by Fichter, Kieffer, and Bernoulli's method (*Ber.*, 1909, **42**, 4710). The acid chloride was then added to zinc ethyl iodide, and the moderate yield of ketonic fraction obtained was converted into the semicarbazone, which crystallised from methyl alcohol in anthracene-like plates, m. p. 162°, identical with the compound isolated from homomesitone (Found: C, 59·2; H, 9·3. Calc. for $C_9H_{17}ON_3$: C, 59·0; H, 9·3%). The regenerated ketone, *ε-methyl-Δ^δ-hepten-γ-one*, had b. p. 66°/18 mm., 53—54°/8 mm., $d_4^{21.5°}$ 0·85516, $n_D^{21.5°}$ 1·45073, $[R_L]_D$ 39·69 (calc., 38·72); its odour was strong and not very pleasant.

Isolation of Ketone (II).—Numerous attempts to obtain this ketone from β-methyl-Δ^β-pentenoic acid (Kon and Linstead, *loc. cit.*) by the action of zinc ethyl iodide on the chloride or of magnesium ethyl iodide on the amide were fruitless, although in the latter case a small amount of liquid with a ketonic smell was obtained but could not be purified. The chloride of the acid* was allowed to react with ethyl sodiomethylacetoacetate in ethereal solution, a good yield of the new ester, CHMe:CMe·CH_2·CO·CMe(CO_2Et)·COMe b. p. 158—168°/19 mm., being obtained; this was hydrolysed by boiling with 10% alcoholic sodium hydroxide for ½ hour, and the ketone formed isolated by distillation in steam: b. p. 74—76°/27 mm., $d_4^{20.4°}$ 0·85595, $n_D^{20.4°}$ 1·4453, $[R_L]_D$ 39·24. The semicarbazone was crystallised from methyl alcohol, and the resulting plates, m. p. 162°, were identified as the αβ-compound, showing that equilibration of the ketone had taken place during hydrolysis.

The ketone was finally isolated by treating the equilibrium mixture from the sodium ethoxide condensation with aluminium

* It should be noted that the acid prepared by the action of sulphuric acid on the hydroxy-acid (*loc. cit.*) contains some αβ-acid. The purest acid is obtained by the cold hydrolysis of the ester obtained by dehydrating the hydroxy-ester with phosphorus oxychloride or potassium hydrogen sulphate. The use of phosphorus pentoxide leads to a mixture of esters.

amalgam (Harries and Eschenbach, *Ber.*, 1896, **29**, 380), whereby the αβ-ketone was reduced to a high-boiling bimolecular condensation product; the unchanged βγ-ketone was then isolated by careful fractionation. The reduction was carried out twice to ensure the complete removal of the αβ-ketone, although the iodine addition of the product did not change. The new compound, *ε-methyl-Δ^ε-hepten-γ-one*, thus obtained had b. p. 63°/19 mm., $d_{4^\circ}^{20\cdot2^\circ}$ 0·85244, $n_D^{20\cdot2^\circ}$ 1·43668, $[R_L]_D$ 38·73 (calc., 38·72); the odour of the ketone was more pleasant than that of the αβ-ketone and quite distinctive. Several different preparations had very similar properties and no saturated ketone, $C_8H_{16}O$, appeared to be produced in the reduction. The *semicarbazone*, although readily formed, was soluble and difficult to purify; it separated from methyl alcohol or ethyl acetate in indefinitely crystalline nodules, m. p. 134° (Found: N, 23·2. $C_9H_{17}ON_3$ requires N, 22·9%).

Equilibrium between the Ketones (I) and (II).—Mixtures of the two ketones were analysed iodometrically with the aid of a reference curve, constructed from the following figures:

Mixture (% αβ-)	0	10	25	50	75	90	100
% Iodine addition	75·3	71·6	64·2	48·7	29·4	16·2	7·8

the αβ-ketone used being regenerated from the pure semicarbazone; the βγ-ketone was the specimen described above.

1. *Point of equilibrium.* The βγ-ketone was treated with hot sodium methoxide for 6 hours and gave a product, $d_{4^\circ}^{20\cdot2^\circ}$ 0·85898, $n_D^{20\cdot2}$ 1·4442, iodine addition 38·8%; on further treatment the value dropped to 35·4 and then remained constant. The ketone prepared by the method of Bodroux and Taboury and purified by regeneration from the semicarbazone was similarly treated and found to have the same iodine addition (35·3%). The composition of this mixture is 67·5% αβ-ketone. This incidentally proved that the βγ-ketone used was free from saturated impurities, otherwise a lower % addition of iodine would have been observed on complete equilibration.

2. *Mobility.* An exactly *N*-solution of sodium in methyl alcohol was added to each of the ketones in molecular proportion; the two mixtures were kept in a thermostat at 25°, and portions withdrawn at intervals for analysis gave the following result:

Initial material:			αβ-Ketone.				
Time (hours)	1	2	3	5	7	28	72
% Iodine addition	21·80	24·49	26·35	29·10	27·47	32·20	35·05
% αβ-Ketone	84·0	80·75	78·75	77·75	77·25	72·00	67·75

Initial material:			βγ-Ketone.			
Time (hours)	1	2	4	6	8	28
% *Iodine addition*	*59·95*	*53·05*	*45·10*	*41·30*	*39·10*	*35·80*
% αβ-Ketone	32·50	44·00	55·00	60·25	63·00	67·00

Ketone, $C_8H_{14}O$, *from Ethyl Ethoxycrotonate and Magnesium Ethyl Iodide*.—Blaise and Maire's preparation (*loc. cit.*) was repeated. The ketonic fraction (obtained in extremely poor yield) was treated with semicarbazide, and the resulting semicarbazone crystallised in small plates which did not felt together; it melted at 158° after several crystallisations from methyl alcohol and was not identical with any of the semicarbazones isolated in the course of this work. The ketone regenerated from it differed from the ketone (I) in smell, although its properties were otherwise very similar: b. p. 49°/8 mm., $d_{4^\circ}^{15 \cdot 8^\circ}$ 0·86004, $n_D^{15 \cdot 8^\circ}$ 1·45233, $[R_L]_D$ 39·58; it gave the same semicarbazone on recombining with semicarbazide. The high molecular refraction and low iodine value indicate an αβ-structure, but the quantity at our disposal did not allow of more thorough investigation.

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CCCXXXIV.—*The Chemistry of Aromadendrene. Part I.*

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DURING the course of his investigations, the late H. G. Smith recorded the presence of a sesquiterpene fraction in the oils obtained from about 140 species of the genus *Eucalyptus* (Baker and Smith, "A Research on the Eucalypts," Sydney, 1920, pp. 336—348), and he expressed the opinion (*op. cit.*, p. 417; *Proc. Roy. Soc. New South Wales*, 1901, **35**, 124) that aromadendrene is the only sesquiterpene present in eucalyptus oils. The largest amounts of aromadendrene were obtained from the oils of *E. nova-angelica* and *E. hæmastoma*, but a considerable quantity was also found to be present in those of *E. Dawsoni*, *E. eximia*, *E. trachyophloia*, *E. affinis*, *E. Maclurata*, *E. cebra*, *E. viminalis*, and *E. acmenoides*. It is probable that this sesquiterpene occurs in the oils of other genera, and it has been suggested tentatively that it is present in those obtained from *Angophora lanceolata* (Smith, *op. cit.*, pp. 17, 418), *Pinus Lambertiana*, Dougl. (Schorger, *U.S. Dept. of Agric. Forest Serv. Bull.*, 1913, No. 119), *Hypericum perforatum*, L. (Zellner, *Arch. Pharm.*, 1925, **263**, 161), *Leptospermum flavescens var. grandiflorum*, Bentham (Penfold, *Proc. Roy. Soc. New South Wales*, 1920, **54**, 198), *L. odoratum*, Cheel

(*idem*, *ibid*., p. 205), *L. flavescens*, Smith (*idem*, *ibid*., 1921, **55**, 171), *L. ericoides* (Johnson and Short, *Rep. Austr. Assoc. Sci.*, 1923, **16**, 220), *L. scoparium* (Short, *J. Soc. Chem. Ind.*, 1926, **45**, 96T), and *L. lanigerum*, Smith (Penfold, *Proc. Roy. Soc. New South Wales*, 1926, **60**, 79).

No solid derivatives of aromadendrene have hitherto been obtained, and for its identification it has been necessary to rely upon the physical constants and upon certain colour reactions, such as that produced by bromine in acetic acid solution. The same colour reactions are, however, exhibited by several dicyclic sesquiterpenes (*e.g.*, gaujene and eudesmene), so they are of very little diagnostic value.*

The purest specimen of aromadendrene isolated by Smith (*op. cit.*, pp. 46, 416) was obtained from the oil of *E. nova-angelica* and had the following physical constants: b. p. 124—125°/10 mm., $[\alpha]_D$ +4·7°, $n_D^{20°}$ 1·4964, $d_{15°}^{15°}$ 0·9222, $[R_L]_D$ 64·89 (calc. for a dicyclic sesquiterpene, 66·14; for a tricyclic sesquiterpene, 64·40). Semmler ("Ätherischen Öle," 1906, *II*, 530) suggested that aromadendrene is not an individual substance but possibly consists of a mixture of di- and tri-cyclic sesquiterpenes. In view of Semmler's criticism, and owing to the fact that no derivatives of aromadendrene had been obtained, it was impossible to establish definitely its identity with the sesquiterpene obtained by one of us (*loc. cit.*) from *Leptospermum* oils until further knowledge of the chemistry of aromadendrene had been acquired; such an investigation has now been made possible by the kindness of Mr. A. R. Penfold, Curator of the Technological Museum, Sydney, who supplied us with 1 lb. of an authentic sample of the oil of *E. nova-angelica*.

The sesquiterpene fraction of this oil was repeatedly fractionated in a vacuum over sodium–potassium alloy, a Widmer column being employed. The fractionation was controlled by determination of the refractive indices and optical rotations of the fractions, rather than by observation of the boiling ranges. After about twenty distillations, the sesquiterpene fraction was collected in two main fractions (representing about 20% of the original oil) and their physical constants (see p. 2527) pointed to the conclusion that the bulk of the sesquiterpene fraction consisted of a single tricyclic sesquiterpene exhibiting an exaltation of approximately one unit in its molecular refractive power. This conclusion has been verified by the preparation of a *dihydroaromadendrene* by exhaustive hydrogenation of the sesquiterpene by the methods of Skita and Paal. Both methods yielded the same result, so that isomerisation during

* Since the sesquiterpene alcohol eudesmol occurs in many eucalyptus oils, it may be anticipated that some of them will also contain eudesmene.

the hydrogenation is improbable. Since the dihydroaromadendren also showed an exaltation of one unit in molecular refractive powe it is evident that the exaltation exhibited by the sesquiterpene i due to some structural peculiarity and not to its contamination wit dicyclic sesquiterpenes. In this respect aromadendrene resemble the tricyclic sesquiterpenes α-gurjunene (Semmler and Spornitz *Ber.*, 1914, **47**, 1151) and copaene (Semmler and Stenzel, *ibid.* p. 2555). It is probable, therefore, that aromadendrene contain either a *cyclo*propane ring conjugated with a double bond (as ir sabinene) together with a *cyclo*butane ring, or, less probably, twc *cyclo*propane rings.

Attempts to obtain solid addition products (nitrosite, nitrosate nitrosochloride) from aromadendrene have not been successful. The hydrochloride, having approximately the composition $C_{15}H_{25}Cl$, is a liquid which cannot be distilled in a vacuum without considerable decomposition.

Dehydrogenation of aromadendrene with sulphur yielded a deep blue oil (b. p. 122—165°/12 mm.) from which no naphthalene hydrocarbon could be obtained, although a small quantity of a black picrate (azulene picrate ?) was isolated from it. Aromadendrene therefore resembles the other tricyclic sesquiterpenes, with the exception of copaene (Henderson, M'Nab, and Robertson, J., 1926, 3077), in its inability to yield a naphthalene hydrocarbon on dehydrogenation with sulphur (Ruzicka, Stoll, Liebl, and Pontalti, *Helv. Chim. Acta*, 1923, **6**, 846).

Ozonisation of aromadendrene in acetic acid solution produced a compound, $C_{14}H_{22}O$ (m. p. 80—81°), approximately the same yield (60%) being obtained from each of the fractions above. This substance formed an *oxime* and a *semicarbazone*, and was at first considered to be an aldehyde, since, even when recrystallised to constant m. p., it reduced Tollens's reagent. The reduction, however, must have been due to contamination with traces of an impurity (probably formaldehyde), since the compound was devoid of reducing properties after it had been regenerated from its oxime. Moreover, the oxime did not yield a nitrile when it was digested with acetic anhydride. It therefore appears that the compound $C_{14}H_{22}O$ is a ketone, and we propose to call it *aromadendrone*.

Aromadendrone did not yield an enol-acetate when boiled with acetic anhydride and sodium acetate. This indicates that the carbonyl group is either situated in the side-chain or attached to two quaternary carbon atoms in the nucleus.

The results so far obtained indicate that aromadendrene is a tricyclic sesquiterpene, which probably contains a *cyclo*hexane nucleus with two bridges and is therefore allied in structure to

α-santalene (Semmler, *Ber.*, 1910, **43**, 446, 1898) and to longifolene (Simonsen, J., 1923, **123**, 2642). The results of ozonisation clearly show the presence of the group C·C(:CH_2)·C.

EXPERIMENTAL.

The fractions referred to on p. 2525 had the following properties: (1) b. p. 121°/10 mm., $[\alpha]_{577}^{20°}$ − 6·1°, $d_{4°}^{20°}$ 0·9116, $n_D^{20°}$ 1·4978, $[R_L]_D$ 65·58; (2) b. p. 121—121·4°/10 mm., $[\alpha]_{577}^{20°}$ ± 0°, $d_{4°}^{17°}$ 0·9157, $n_D^{17°}$ 1·4993, $[R_L]_D$ 65·44 [Found, for (1): C, 88·3; H, 11·8; for (2): C, 88·2; H, 11·9. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%. $[R_L]_D$ for a dicyclic sesquiterpene, 66·14; for a tricyclic sesquiterpene, 64·40].

In addition to these two fractions a small first-running ($n_D^{20°}$ 1·4974, $[\alpha]_{577}^{20°}$ − 13·6°) and a small fraction (b. p. 124°/10·3 mm., $n_D^{20°}$ 1·4989, $[\alpha]_{577}^{20°}$ + 0·59°) were also obtained.

Hydrogenation.—(1) 12 G. of aromadendrene (fraction 2, freshly distilled over sodium), dissolved in pure methyl alcohol (200 c.c.), were hydrogenated in presence of 0·05% of colloidal palladium (Paal and Gerum, *Ber.*, 1908, **41**, 809) in the apparatus described by Skita and Meyer (*Ber.*, 1912, **45**, 3594), hydrogen from a cylinder being passed at slightly above atmospheric pressure for 20 hours. The product was poured into water, extracted with ether, dried, and distilled over sodium. The hydrogenation was then repeated with a further quantity of colloidal palladium (0·05%) and was found to be complete. The product, extracted in the usual way, was distilled over sodium, and practically the whole passed over at 121—122°/10 mm. (Found: C, 87·2; H, 12·7. $C_{15}H_{26}$ requires C, 87·4; H, 12·6%). *Dihydroaromadendrene* is a colourless oil having $d_{4°}^{17°}$ 0·9014, $n_D^{17°}$ 1·4871, $[R_L]_D$ 65·83 (calc. for a tricyclic dihydrosesquiterpene, 64·87).

(2) *Aromadendrene (fraction 2) was also exhaustively hydrogenated* by Skita's inoculation method (*loc. cit.*). Addition of the inoculating solution to the aromadendrene–platinic chloride mixture and subsequent passage of hydrogen tended to yield a granular rather than a colloidal precipitate, and the hydrocarbon was therefore added after the colloidal condition had been induced. The aromadendrene (10·7 g.) was reduced in presence of colloidal platinum (0·95 g.), water (84 g.), and purified acetic acid (200 c.c.) at an excess pressure of 0·25 atm. Absorption of hydrogen ceased after about 6 hours and no further absorption occurred on the addition of more colloidal platinum. The purified product (Found: C, 87·4; H, 12·6%) had b. p. 115—116°/8—9 mm., $n_D^{22°}$ 1·4847, $d_{4°}^{22°}$ 0·8972, $[R_L]_D$ 65·71.

Dehydrogenation.—Aromadendrene (8 g.; fraction 1) and sulphur

(4 g.) were heated together for 4 hours, during which the temperatu was slowly raised from 210° to 290° and the evolution of hydrog sulphide was completed. The reaction mixture was then distill and purified by redistillation from potassium in a vacuum. Tl distillate (b. p. 122—165°/12 mm.) was a deep indigo-blue oil, fro which no naphthalene hydrocarbon could be isolated (as picrate but which yielded a trace of a black substance (m. p. 114—116° possibly identical with eucazulene picrate (Ruzicka and Rudolp *Helv. Chim. Acta*, 1926, **9**, 118).

Aromadendrone.—A solution of aromadendrene (13 g.) in glaci acetic acid (60 c.c.) was cooled in ice-water and treated with a strea of ozonised oxygen (approx. 14% O_3) until a test portion no long decolorised a dilute solution of bromine in acetic acid (2·5 hour The straw-coloured liquid was concentrated under diminish pressure at 50—60° to half its volume, cautiously heated un incipient decomposition was observed, and the flask was then cool in water to moderate the strongly exothermic reaction which to place. In the first experiments the ketone was recovered by stean distillation, but it was subsequently found better to pour the co residue into about six times its volume of ice-water, for the crystalli ketone then separated at once and could be filtered off. Th filtrate, on neutralisation, deposited a small quantity (0·55 g.) an amorphous, white solid which was not further examine Crystallisation of the crude ketone (11·7 g.) from dilute aceto yielded 5 g. of pure substance, and another 3 g. were obtained recrystallisation of the fraction of the mother-liquor boiling betwe 142·5° and 150°/10 mm. (total yield, 61%).

Aromadendrone crystallises in feathery, white needles (m. 80—81°) having a characteristic odour, and is very soluble in meth and ethyl alcohols, chloroform, and acetone. It may be recrysta lised from 60% alcohol or from acetone by dilution with wat (Found: C, 81·4; H, 10·7; *M*, cryoscopic in benzene, 208· 207·6. $C_{14}H_{22}O$ requires C, 81·6; H, 10·7%; *M*, 206).

The *oxime* was obtained in almost theoretical yield by the inte action of aromadendrone with twice the theoretical quantities hydroxylamine hydrochloride and sodium bicarbonate in 95 alcohol (44 hours at 56°). It crystallises in needles (m. p. 103°) fro methyl alcohol (Found: N, 6·5, 6·4. $C_{14}H_{23}ON$ requires N, 6·3%)

The *semicarbazone*, m. p. 189·5—190·5° (decomp.), prepare in the usual way, is a microcrystalline powder (from hot meth alcohol) which is difficult to purify (Found: N, 15·7. $C_{15}H_{25}ON$ requires N, 16·0%).

Dehydration of the Oxime.—The oxime was boiled (1·25 hours) wit twice its weight of purified acetic anhydride. The dark-coloure

product was worked up in the usual way, but yielded fractions of high boiling-point instead of a nitrile.

Aromadendrone and Acetic Anhydride.—The ketone (5 g.), purified acetic anhydride (10 g.), and fused sodium acetate (0·5 g.) were boiled together for ¾ hour. The product was cooled, shaken with water, and the crystals which separated were taken up in ether, washed with dilute sodium carbonate, dried, and distilled. Almost the whole passed over at 141—144°/10 mm., and the pure ketone (4 g.) was recovered from this fraction.

One of us (W. F. S.) wishes gratefully to acknowledge the receipt of a grant from the New Zealand Institute which enabled him to purchase the ozoniser and hydrogenation and micro-analytical apparatus. Our thanks are due to the Chemical Society for the ›an of a vacuum pump, and to the authorities administering the ›uffus Lubecki Fund for a scholarship which enabled one of us ʟ. H. B.) to participate in this investigation.

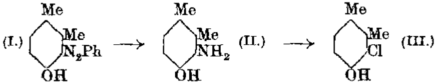
UNIVERSITY COLLEGE,
AUCKLAND, NEW ZEALAND. [*Received, July 23rd,* 1928.]

'CCXXXV.—*Chloro-*o*-xylenols. Part II. 3-Chloro-*o*-4-xylenol, the Dichloro-*o*-4-xylenols and 4 : 5-Dichloro-*o*-3-xylenol.*

›y LEONARD ERIC HINKEL, ERNEST EDWARD AYLING, and LILIAN COLLIER BEVAN.

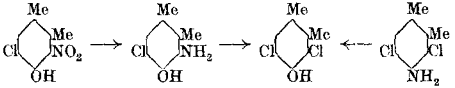
› previous communications (J., 1923, **123**, 2968; 1924, **125**, 1847) x chloro-*o*-xylenols have been described; the syntheses of five ' the eight remaining chloro-*o*-xylenols have now been completed.

The synthesis of 3-chloro-*o*-4-xylenol was achieved through 4-xylenol, which was coupled with benzenediazonium chloride)iepolder, *Ber.*, 1909, **42**, 2918; 1911, **44**, 2498), the 3-benzeneazo-4-xylenol (I) being separated from the accompanying 5-benzene-zo-*o*-4-xylenol, and reduced to 3-*amino*-o-4-*xylenol* (II), which was ›nverted into 3-*chloro*-o-4-*xylenol* (III) in the normal manner.



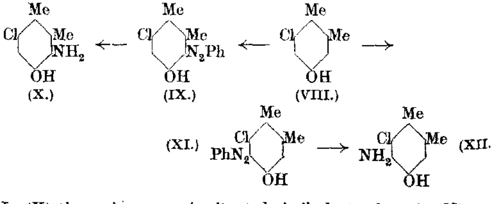
3 : 5-*Dichloro*-o-4-*xylenol* was synthesised through 5-chloro-*o*-4-ʏlenol (Hinkel, Collins, and Ayling, J., 1923, **123**, 2973). The tter did not couple with benzenediazonium chloride, and was

therefore nitrated, and the resulting 5-*chloro*-3-*nitro*-o-4-*xylenol* (IV) reduced to 5-*chloro*-3-*amino*-o-4-*xylenol* (V). Replacement of the amino-group by chlorine did not yield a homogeneous product, although the similar action with 3-amino-*o*-4-xylenol (II) proceeded normally. The mixture of chloro-xylenols obtained from (V) probably resulted from either a partial elimination of the amino-group or its partial replacement by a second hydroxyl group instead of by chlorine. From the mixture a pure dichloro-*o*-4-xylenol was isolated, which was identical with 3 : 5-dichloro-*o*-4-xylenol (VI) subsequently prepared from 3 : 5-dichloro-*o*-4-xylidine (VII) (this vol., p. 1878), thus confirming the position of the nitro-group in (IV).



(IV.) (V.) (VI.) (VII.)

In an attempted synthesis of 5 : 6-dichloro-*o*-4-xylenol, 6-chloro-*o*-4-xylenol (VIII) (Hinkel, J., 1924, **125**, 1852) was coupled with benzenediazonium chloride, and the resulting azo-compound reduced to the corresponding amine, but attempted replacement of the amino-group by chlorine resulted in its unexpected elimination with regeneration of the starting material. Since, in the latter, both ortho-positions to the hydroxyl group are free, the coupling of the diazonium chloride can yield either of the azo-compounds (IX) and (XI), the product on reduction being either of the amines (X) and (XII).



In (X) the amino-group is situated similarly to those in (II) an (V), in which the amino-group can be replaced by chlorine. Th serves in a measure to establish the constitutions of the azo-con pound and the amine as 5-*benzeneazo*- (XI) and 5-*amino*-6-*chloro*-o-*xylenol* (XII) respectively, and the fact that 5-chloro-*o*-4-xylen does not couple with benzenediazonium chloride (compare p. 252

whilst *o*-4-xylenol couples mainly in position 5 (compare Diepolder, *loc. cit.*), supports this view.

5 : 6-Dichloro-*o*-4-xylenol was finally prepared from 5 : 6-dichloro-*o*-4-xylidine (this vol., p. 1877) and is identical with the compound described by Hinkel (J., 1924, **125**, 1851).

4 : 5-*Dichloro*-o-3-*xylenol* and 3 : 6-*dichloro*-o-4-*xylenol* were prepared similarly from the respective dichloro-xylidines (this vol., p. 1876), although in no case does the replacement of the amino-group proceed smoothly.

EXPERIMENTAL.

3-*Amino*-o-4-*xylenol*.—3-Benzeneazo-*o*-4-xylenol, prepared according to Diepolder (*loc. cit.*), was finally purified by several crystallisations from light petroleum (b. p. 60—80°) and obtained as dark red crystals, m. p. 70°. The azo-compound was reduced in alcoholic solution with sodium hydrosulphite, and on removal of the alcohol under reduced pressure, a white solid separated which crystallised from benzene in small crystals, m. p. 126° (Found : N, 10·2. $C_8H_{11}ON$ requires N, 10·2%).

3-*Chloro*-o-4-*xylenol*.—3-Amino-*o*-4-xylenol was diazotised and treated with cuprous chloride in the usual way. Distillation with steam yielded an oil, which was extracted with ether, and the extract washed with sodium hydroxide solution. The xylenol, recovered from the alkaline solution by acidification and extraction with ether, crystallised from light petroleum (b. p. 40—60°) in transparent crystals, m. p. 27° (Found : Cl, 22·4. C_8H_9OCl requires Cl, 22·7%). The *benzoyl* derivative, prepared in the usual manner, crystallised from dilute alcohol in prisms, m. p. 87° (Found : Cl, 13·4. $C_{15}H_{13}O_2Cl$ requires Cl, 13·6%).

5-*Chloro*-3-*nitro*-o-4-*xylenol*.—To 1 g. of 5-chloro-*o*-4-xylenol (Hinkel, Collins, and Ayling, *loc. cit.*) in 10 c.c. of glacial acetic acid, 0·5 c.c. of nitric acid in 10 c.c. of glacial acetic acid was slowly added. After standing for 20 minutes, the mixture was poured on ice, and the precipitated solid distilled in steam. The solid distillate crystallised from benzene in yellow plates, m. p. 127·5° (Found : Cl, 17·6. $C_8H_8O_3NCl$ requires Cl, 17·6%).

5-*Chloro*-3-*amino*-o-4-*xylenol*.—5-Chloro-3-nitro-*o*-4-xylenol was reduced in alcoholic solution with sodium hydrosulphite. On removal of the alcohol under reduced pressure, a white solid was precipitated which crystallised from alcohol in very fine needles, m. p. 175°, with considerable darkening just below the m. p. (Found : Cl, 20·3. $C_8H_{10}ONCl$ requires 20·7%).

3 : 5-*Dichloro*-o-4-*xylenol*.—(1) 5-Chloro-3-amino-*o*-4-xylenol (2 g. in 240 c.c. of hydrochloric acid) was diazotised at 0°, poured into

cuprous chloride solution, distilled with steam, and the distillate extracted with ether. The extract was washed with sodium hydroxide solution, and the alkaline solution yielded a mixture of xylenols which, on fractional crystallisation from light petroleum (b. p. 60—80°), yielded mainly 3 : 5-*dichloro*-o-4-*xylenol as feathery crystals*, m. p. 52°, *the constitution being confirmed by the synthesis described below (Found: Cl, 36·8.* $C_8H_8OCl_2$ *requires Cl, 37·2%).* The *benzoyl* derivative crystallised from light petroleum (b. p. 40—60°) as white crystals, m. p. 89° (Found: Cl, 23·6. $C_{15}H_{12}O_2Cl_2$ requires Cl, 24·1%).

(2) 3 : 5-Dichloro-*o*-4-xylidine (this vol., p. 1878), dissolved in concentrated sulphuric acid, was diazotised at 0°, poured into dilute sulphuric acid, and steam-distilled. The distillate, which consisted mainly of 3 : 5-dichloro-*o*-xylene (4 : 6-dinitro-derivative, m. p. 175°; compare Crossley and Renouf, J., 1904, **85**, 284) together with a small quantity of the xylenol, was extracted with ether, and the extract washed with sodium hydroxide solution. The xylenol, obtained from the alkaline solution in the usual manner and purified from light petroleum (b. p. 60—80°), was identical with the 3 : 5-dichloro-*o*-4-xylenol described above.

6-*Chloro*-5-*benzeneazo*-o-4-*xylenol*.—The requisite amount of benzenediazonium chloride solution was coupled with 2·6 g. of 6-chloro-*o*-4-xylenol (Hinkel, *loc. cit.*) in slightly alkaline solution The precipitate crystallised from alcohol in red needles, m. p. 143° (Found: Cl, 13·6. $C_{14}H_{13}ON_2Cl$ requires Cl, 13·4%).

6-*Chloro*-5-*amino*-o-4-*xylenol*.—The foregoing azo-compound was reduced in aqueous-alcoholic solution with sodium hydrosulphite removal of the alcohol under reduced pressure precipitated a whit solid, which crystallised from dilute alcohol in fluffy needles m. p. 144·5° (Found: Cl, 20·1. $C_8H_{10}ONCl$ requires Cl, 20·7%) Diazotisation of the amine and treatment with cuprous chloride in the usual manner, followed by distillation with steam, yielded white solid, which was extracted with ether, and then crystallise from light petroleum (b. p. 60—80°) in fine needles, m. p. 98° unchanged by admixture with 6-chloro-*o*-4-xylenol, m. p. 98°.

5 : 6-*Dichloro*-o-4-*xylenol*.—5 : 6-Dichloro-*o*-4-xylidine (this vol p. 1877), 0·5 g. at a time, was dissolved in 5 c.c. of sulphuric acid; th sulphate was precipitated in a finely divided state by the additic of 10 c.c. of water, diazotised at 0°, and gently warmed to 40° unt a clear solution was obtained. The diazotised solution was treate according to the method of Heinichen (*Annalen*, 1889, **253**, 28 compare Cain and Norman, J., 1906, **89**, 19) by the addition 20 c.c. of concentrated sulphuric acid, but modified by heating t acid solution for 1 hour on a steam-bath. Other methods of trea

nent (compare Cain and Norman) result in the formation of much ·ed solid, which is reduced to a minimum by the above procedure. The acid solution was distilled with steam, the solid distillate treated vith dilute sodium hydroxide solution, the solution filtered, and the xylenol recovered in the usual manner; it crystallised from well-·ooled light petroleum (b. p. 60—80°) in tiny rosettes, m. p. 102·5° Found: Cl, 36·6. Calc. for $C_8H_8OCl_2$: Cl, 37·2%). The benzoyl lerivative crystallised from dilute alcohol in stellate groups, m. p. ?7·5° (Found: Cl, 23·8. Calc. for $C_{15}H_{12}O_2Cl_2$: Cl, 24·1%). These n. p.'s were unchanged by admixture with the corresponding ·ompounds described by Hinkel (J., 1924, **125**, 1851).

3 : 6-*Dichloro*-o-4-*xylenol*.—3 : 6-Dichloro-*o*-4-xylidine (this vol., ›. 1878) was dissolved by heating in 30% sulphuric acid. The finely livided sulphate obtained on cooling was diazotised at 40°, poured nto boiling 40% sulphuric acid, and distilled with steam. The olid distillate was treated with dilute sodium hydroxide solution, he solution filtered, acidified, and extracted with light petroleum b. p. 40—60°). The xylenol crystallised in long, flat needles, m. p. ›4° (Found: Cl, 36·8. $C_8H_8OCl_2$ requires Cl, 37·2%). The *benzoyl* lerivative crystallised from methyl alcohol in transparent, flat needles, m. p. 124° (Found: Cl, 23·8. $C_{15}H_{12}O_2Cl_2$ requires Cl, ?4·1%).

4 : 5-*Dichloro*-o-3-*xylenol*.—4 : 5-Dichloro-*o*-3-xylidine (this vol., ›. 1876) was treated exactly as in the preceding case, and the ·ylenol, recovered in the usual manner, crystallised from light ›etroleum (b. p. 60—80°) in stellate masses, m. p. 90° (Found: Cl, 36·5. $C_8H_8OCl_2$ requires Cl, 37·2%). The *benzoyl* derivative rystallised from dilute alcohol in prisms, m. p. 133° (Found: Cl, 24·3. $C_{15}H_{12}O_2Cl_2$ requires Cl, 24·1%).

UNIVERSITY COLLEGE, SWANSEA. [*Received, July 24th*, 1928.]

CCCXXXVI.—*The Conditions determining the Thermodynamic Stability of Cyanohydrins of Carbonyl Compounds. Part I. Some Effects of* (a) *Substitution in Aromatic Aldehydes and* (b) *Ring Formation.*

By ARTHUR LAPWORTH and RICHARD HELMUTH FRED MANSKE.

INCE the condition of equilibrium attained by a system underoing a reversible thermal chemical change is subservient to the aws of thermodynamics and independent of considerations such as

the relative velocities of the reactions by which the final sta attained, it follows that any factor connected with the constitu of one or more of the molecular species concerned, which is f to produce a definite alteration in the condition of equilibriu one which affects the "static" or average condition of the vidual molecules. The adjective "*static*" is here used with recognition of the principle that there is always a great varie deviations from the average.

In recent discussions of the theory of mechanism of reactio carbon compounds, there has been evident a tendency to re some of the factors which control chemical change as opera primarily on reaction velocity and others on the conditio equilibrium. Among the factors which have been most frequ considered are those to which Flürscheim originally applie distinguishing terms "quantitative" and "electropolar" (com J., 1909, **95**, 725). These two terms are retained throughou present paper, being regarded as defined, not by any special h thesis, but rather by the practical criteria originally laid dow Flürscheim.

The work of Victor Meyer and his pupils revealed the depre effect of ortho-substituents on the rates of hydrolysis of be esters. Flürscheim showed that all substituents when prese the ortho-position also have the effect of raising the ionis constant of benzoic acids, no matter what the signs of the q titative and electropolar factors. He attempted to account fo kind of effect by the introduction of a theory which had a ki basis (*loc. cit.*). His explanation still has a wide popularity is not accepted by the present authors, for it virtually postula mechanism by the automatic operation of which the second la thermodynamics is rendered inoperative; the case is, in fact in which the principle restated in the foregoing paragraphs ca usefully applied. Since the ionisation constant of an acid a given temperature and pressure and in any given solvent is si a function of the increase in the free energy which is asso with the complete ionisation (including any simultaneous cl of solvation) of 1 g.-mol. of the un-ionised acid as it exists i solution, it is evident that the so-called "steric" factor doe in this instance at least, operate primarily by modifying the at which a given change in entropy occurs, but actually alte chemical potentials or entropies of the individual ions or mol (or both) concerned.

Flürscheim also discovered and demonstrated in convi manner that, not only the so-called "steric" factor, but als quantitative and electropolar factors make themselves felt i

magnitudes of ionisation constants. It follows of necessity that all three factors affect the entropies of the separate molecules or ions or both. The data now given (see Experimental) seem to show beyond doubt that neutral molecules are influenced by all three factors, and it would be unreasonable to assume that the same is not also true of ions.

It should now be clear that, if the alternate effects associated with the factor which Flürscheim termed "quantitative" be admitted to have a polar origin, then it would not be logical to maintain that polar considerations primarily affect reaction velocity (compare E. H. Ingold, J., 1925, **127**, 470).

Evidence obtained during the course of measurements of cyanohydrin equilibria (on which subject the experimental section of the present paper forms the first communication) indicates the operation of other factors which are not conspicuous in the study of ionisation of carboxylic acids or of aromatic substitution. Whilst the substituents NMe_2, OH, OCH_3, Cl, and CH_3 produce on the stability of benzaldehydecyanohydrin effects which are not inconsistent with prevailing views on the modes of operation of their quantitative and electropolar factors, the nitro-group appears out of place (p. 2546). There is already evidence that the nitro-group is not singular among meta-directive substituents in simulating the properties of ortho-para-directive substituents when the practical issue is the reduction in the additive power of a carbonyl group. Thus Mr. Glyn Owen, in these laboratories, has found that the cyanohydrin of benzoylformic ester has a somewhat higher dissociation constant than benzaldehyde, and as it is well known that the carbonyl group of ethyl benzoate has but very feeble additive properties, it is clear that in respect to efficiency in producing such results CO_2Et also comes between H and OEt.

The tendency of two or more double bonds (this term being applied to systems present in ethylenes, in $\cdot NO_2$, ·CO·Alk, and $\cdot CO_2Alk$) to arrange themselves alternately with single bonds indicates that such an arrangement is ordinarily associated with an element of stability (*i.e.*, of large entropy) which must therefore operate unfavourably on any chemical change in which that arrangement is destroyed. There is no reason to believe that this factor is *necessarily* associated with polarisation. It will hereafter be referred to as the "Thiele factor," in view of the circumstance that the term "conjugation" is now commonly applied in a much wider sense. This factor would operate so as to stabilise, though to a quite unknown extent, the carbonyl form in a ketone or aldehyde of the types $CR^1R^2{:}CR^3{\cdot}CR^4{:}O$, $O{:}CR^1{\cdot}CR^2{:}O$, and probably also $NO_2{\cdot}CR{:}O$. This may conceivably account for some

apparent abnormalities in cyanohydrin formation, but there is yet another possibility which must not be overlooked.

The symbol $\underset{\smile\!\nearrow}{\dot{\bar{A}}_0 \overline{} A_1}$, etc., was first used by one of us in an attempt to account for the alternate effects (associated with the quantitative factor) to which such substituents as NMe_2, OEt, CH_3, etc., in position A_0 give rise when they are attached directly to carbon in position A_1 in certain atomic assemblages. The symbol *implied* (1) *an increase in the covalence* between A_0 and A_1, and (2) a movement of Faraday tubes equivalent to a drift or displacement of electrons, relatively to nuclei, in the direction indicated by the arrow.

The view may now be expressed that what is here essential is (1) the direction of electron displacement, and (2) the resulting change in the properties of A_1 and the atoms to the right of A_1. If it be assumed, for simplicity in the first instance, that the molecule terminates at A_1, the operation suggested in the figure would clearly imply that the nucleus of A_1 is engaged with an increased share of electrons, and consequently the restraint which it can exercise over its proper valency electrons must diminish, much as if some of its central charge has been removed. The "fugacity" of the valency electrons of A_1 has increased.

It is not apparent that there is any mode of ascertaining how far an observed change in the restraint on the valency electrons of an atom caused by replacement of H by A_0 (when A_0 is, for example, CH_3) can be ascribed to change in the value of the covalency, how far to simple electron displacement relative to nuclei (electron drift), or how far to an external electrostatic field, such as one arising out of the formation of the arrangement A_0—A_1, etc., from H—A_1, etc. It is rather the *sum total* of these which we may hope to detect, and possibly to estimate roughly, by observing either *the change in the properties of* A_1 *or the consequent effects of this* change on the rest of the molecule. The latter method was in principle the practical basis of the criteria used by Flürscheim.

Henceforward, therefore, the modified form $\underset{\Sigma\!-\!\nearrow}{\dot{\bar{A}}\text{—}A_1}$, etc., will be used to denote an arrangement in which the replacement of H in H—A_1, etc., by A_0 produces, *by all effects from the left combined* (as indicated by Σ), an increase in the fugacity of the valency *electrons of* A_1, and this will be termed the "primary" interior effect of the substitution process. It is held that the classification of substituents based on Flürscheim's criterion for the quantitative factors gave the most satisfactory means hitherto discovered of *ascertaining primary interior effects, i.e.*, of ascertaining whether,

and roughly to what relative extent, a given substituent normally increases or decreases the fugacity of the valency electrons of a tervalent carbon atom at which substitution occurs. Those substituents, like NMe_2, OEt, Cl, and alkyl, which produce the same type of quantitative effect as a negative charge would do, are supposed to be those which by such substitution raise, on the whole, the fugacity of the electrons of A_1, when A_1 is a tervalent * or bivalent carbon atom. Substituents such as NO_2, CO·R, and NMe_3^+ in place of A_0 are imagined to be those which in their totalised effect on A_1 (where A_1 is tervalent or bivalent carbon) reduce the fugacity of its valency electrons.

It should be noted that the hypothesis above defined has definite reference to effects on tervalent and bivalent carbon only. Evidence as to how such groups as NMe_2, OH, or OAlk affect the restraint on valency electrons of an attached saturated (quadrivalent) carbon atom is not conclusive, but the change is certainly small. It is the *difference* between the effects on quadrivalent and tervalent or between tervalent and bivalent carbon to which attention must be paid in considering the stability of covalence attachments.

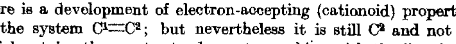
In connexion with the stability of the cyanohydrins of aldehydes and ketones, Robinson and Rây have explained how a substituent which increases the fugacity of the electrons of the carbon atom of a carbonyl group virtually endows that atom with an increased negativity, which must tend to decrease its attraction for negative ions such as CN^- (J., 1925, **127**, 1610). The present authors concur in this idea in so far as the electrostatic attraction is concerned, but suggest that something even more far-reaching may be postulated.

It has been suggested above that introduction of a substituent such as NMe_2, OH, OCH_3, Cl, or CH_3 in place of H produces a *totalised* effect on unsaturated carbon which is equivalent to a decrease in the restraint exercised by the central positive charge on the octet. With such an alteration, the atom will tend to display properties approaching those of boron. It follows that those structures in which the atom displays tervalency will become more stable *relatively to those in which it displays quadrivalency*. Consistently with this, the capacity of carbonyl to form stable, neutral, addition

* "Tervalent" is applied in the present paper to an atom which is exercising the co-ordination number 3, in the sense originally intended by Werner. Thus, carbon in ethylene, carbonyl, and carboxyl is described as "tervalent," and carbon in carbon dioxide as "bivalent." This application of such terms is in no way novel (compare Smith's "Inorganic Chemistry," by J. Kendall, G. Bell and Sons, Ltd., 1927, pp. 158—161), and has now been adopted in view of recent tendencies to restrict the use of the term "co-ordination."

products with H·CN, H·OH, and H·NH_2 decreases wherever the present theory, by utilising Flürscheim's criteria, predicts a large increase in the fugacity of the electrons of the carbonyl carbon atom, providing that the constitution of the substituent is not such as to form with the rest of the molecule a system with alternate single and double linkages and, therefore, is not such as to provide the carbonyl compound with an added non-polar element of stability ("Thiele factor," p. 2535). With singly bonded substituents, X in X·CO·R, it may with confidence be stated that the stability of the carbonyl addition products with neutral agents of the type above specified will be found to increase in the order: X = NMe_2, OAlk, Alk, (H). The truth of this is obvious enough in its application to the large contrast between OMe and CH_3 (in esters and ketones) and even to the comparatively small contrast between CH_3 and H, as consideration of the gradation in properties of CH_3·CO·CH_3, H·CO·CH_3, and H·CO·H will show.

If the analogy of changing central restraint suggested above may legitimately be pursued further, it may be inferred that replacement of H in H·C^1R:X by a substituent of the meta-directive type, such as NO_2 or CO·R, would have an effect on the carbon atom C^1 equivalent to an increase in the central charge on the latter. The atom C^1 might be said to show more "positiveness" in consequence of this; but it does not necessarily follow from this that the atom would more readily form a more stable covalency link by combination with a CN^- or OH^- ion. On passing from boron through carbon and nitrogen to oxygen, with increasing nuclear charge the capacity of the atom to exercise the co-ordination number 4 rises to a maximum and then decreases. Similarly, as A_0 in A_0·C^1R:X is replaced successively by NMe_2, OMe, CH_3, H, CO·R, and NO_2, the compound becomes more cationoid, but the relative stability of the addition product in which C^1 is quadrivalent may attain a maximum (not *necessarily* at hydrogen), and then decline. In this connexion it is very significant that on passing from, say,



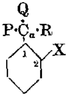
there is a development of electron-accepting (cationoid) properties in the system C^1=C^2; but nevertheless it is still C^2 and not C^1 which retains the greater tendency to combine with the "active" (or carbon-covalence-seeking) part of the agent [CN in HCN; $CH(CO_2Et)_2$ in ethyl sodiomalonate; Ar·N_2 in diazo-compounds; NO_2 in HO·NO_2].

It is desirable that it should be realised from the outset that the primary interior effect of a given substituent on an atom varies,

even in sign, with the nature of the atom at which substitution takes place. Thus, replacement of H in HCl[1] by Cl[2] does not increase the fugacity of the electrons of Cl[1]; on the contrary, the product now shows nothing but strongly electron-seeking properties. Boron, on the other hand, resembles carbon, for while boron, in its hydrides, displays consistent quadrivalency, no neutral chloride is known in which boron displays a valency greater than three.

All ortho-substituents (other than OH) hitherto examined greatly increase the stability of the cyanohydrin group (see Table I), no matter what the quantitative or electropolar factors may be. This is quite irreconcilable with the idea that substituents so placed roduce their effect in virtue of their occupation of space (compare lso Kuhn and Wassermann, *Helv. Chim. Acta*, 1928, **11**, 3 *et seq.*).

In comparing the effects of ortho-substituents on the dissociation onstants of cyanohydrins, on the one hand, and on the onisation of carboxylic acids, on the other, it is natural o observe that both phenomena might at first sight be ccounted for by assuming that a substituent X in osition 2 in the annexed figure decreases the fugacity f electrons of C_a and, therefore (by consequent electron lisplacements), of the electrons of the atoms attached to C_a.



Having regard, however, to the possibility (for which reasons ave been given above) that a large decrease in the fugacity of the lectrons of C_a may not necessarily decrease the capacity of C_a o become quadrivalent, an alternative must not be overlooked. hat alternative is a "direct" effect of X through space on the toms or groups attached to C_a, rather than an effect on C_a itself, nd it must in any case be an effect which both helps C_a to exercise s maximum co-ordination number and reduces the fugacity of he valency electrons of the atoms P, Q, and R attached to C_a; the latter requirement is shown by the decreased ability of the xygen of ortho-substituted benzoic acids to retain a proton.

The most useful and significant measurements of thermodynamic hanges associated with addition reactions of carbonyl compounds re certainly those of Adkins and Adams (*J. Amer. Chem. Soc.*, 925, **47**, 1368), who studied the free energy of the formation of cetals from alcohols and carbonyl compounds, both aldehydes and etones, by means of equilibrium measurements. This reaction, owever, is highly complex, involving at equilibrium six molecules of ur different chemical species:

$$2R'{\cdot}OH + R''{\cdot}CO{\cdot}R''' \longleftrightarrow R''{\cdot}C(OR')_2{\cdot}R''' + 2H_2O.$$

The ideal case for study is no doubt that in which only two

molecules of two chemical species are concerned at equilibrium (exclusive of catalysts), A$\leftrightarrow$A^1, corresponding with the phenomenon of *simple isodynamic change. Next to this in simplicity come* two cases where three molecules are concerned :

$$(a)\quad A + A \leftrightarrow C \text{ (two species)}$$
$$\text{or}\quad (b)\quad A + B \leftrightarrow C \text{ (three species)}.$$

Here, (*a*) would include all the simplest cases of polymerisation and no simpler example of (*b*) could be taken than that of reversible cyanohydrin formation: $R_2CO + HCN \leftrightarrow R_2C(OH)\cdot CN$, which is probably a simpler case than that of oxime or hydrazone formation (Petrenko-Kritschenko, *Ber.*, 1901, **34**, 1702; *Annalen*, 1905, **341** 150; *Ber.*, 1906, **39**, 1454; Fischer, *Annalen*, 1886, **236**, 146 Stewart, J., 1905, **87**, 185, 410) and corresponds more closely with the formation of bisulphite double compounds (Stewart, *loc. cit.*).

Ultée (*Rec. trav. chim.*, 1909, **28**, 248, 257) examined the stability of a number of cyanohydrins, mainly by admixture of an aldehyde or ketone with anhydrous hydrogen cyanide in equimolecular proportion and in absence of solvent. The results were not in a form suitable for quantitative comparison, and this was more especially the case with aliphatic aldehydes, the cyanohydrins of which are so stable that the concentrations of the free hydrogen cyanide and of the free aldehyde (which could only be estimated by difference) were very uncertain. The equilibrium constants calculated for Ultée's liquid systems are not directly comparable with those given in the present paper, which refer to a different medium.

W. J. Jones (*J.*, 1914, **105**, 1560) compared the dissociation constants of one or two cyanohydrins in aqueous solution, and confirmed Ultée's conclusion that in general the formation of cyanohydrins is incomplete, even with aldehydes; he made a quantitative comparison between the values of the equilibrium constant $K = C_{R_2CO} \times C_{HCN}/C_{R_2C(OH)\cdot CN}$ in aqueous solution and found the constant for acetone to be about eleven times as large as that for acetaldehyde.

The present authors have extended this work and made observations with a large number of aldehydes and ketones; but, as water is not generally suitable as a solvent, 96% alcohol was used as the medium throughout. Chemically, the principle on which the measurements were based was the same as that applied by Ultée and by Jones; it has recently been discussed at sufficient length by Lapworth, E. B. Robinson, and Manske (J., 1927, 2052 *et seq.*) and it is only necessary here to give details of the modified procedure adopted during the present research.

EXPERIMENTAL.

Preparation and Purification of the Aldehydes and Ketones.—Exigencies of space make it impracticable to give details for so many different compounds. Where the aldehydes or ketones were solids with a fairly high melting point, the procedure, as a rule, was fairly straightforward, and frequent recrystallisation from suitable solvents was always resorted to in the final stages—as, for example, where a nearly pure sample had been made synthetically or purchased as " pure " from a firm of repute and had passed the necessary preliminary tests satisfactorily. Where the compounds were liquids or low-melting solids, the methods of preparation adopted often afforded the necessary preliminary guarantee of homogeneity, and the elimination of most of the remaining impurities was always attempted by applying Richards's method of repeated distillation, with rejection of large initial and final fractions (compare *J. Amer. Chem. Soc.*, 1912, **34**, 978) even when the boiling-point range of the original material was very narrow. In each fractionation, wherever practicable, only the middle two-thirds of the distillate were utilised, so that when several successive operations were carried out, the proportion ultimately retained was very small. Oxidisable or hygroscopic compounds were fractionated in an atmosphere of dry carbon dioxide and then used immediately with every necessary precaution to avoid access of air or moisture.

In all cases where the aldehyde or ketone gave a crystalline bisulphite compound this was made as a stage in the preparative process.

In the following cases the starting materials used, and subjected to further treatment on the lines above indicated, were the best products made by British Drug Houses, Ltd. : Fluorenone and *o*-chloro-, *o*-nitro-, *m*-hydroxy-, *p*-hydroxy-, and *p*-dimethylamino-benzaldehydes.

The original *p*-nitrobenzaldehyde was purchased from Kahlbaum. In the case of *o*-nitrobenzaldehyde, traces of *o*-nitrosobenzoic acid present were easily removed by two successive precipitations from benzene solution by addition of light petroleum. The crude methoxybenzaldehydes were made by methylating the purified hydroxy-aldehydes; *m*-nitrobenzaldehyde was made by the method described in Erdmann's " Anleitung der Organischen Preparate " (Stuttgart, 1894), and *p*-metboxy-*m*- and -*o*-methylbenzaldehydes were made by the application of Gattermann's process to pure *o*- and *m*-cresol respectively.

Crude *m*-chloro- and *m*- and *p*-methyl-benzaldehydes were obtained from the corresponding chloro- and methyl-benzonitriles by Stephen's process (*J.*, 1925, **127**, 1874). It is worthy of remark

that, owing to the retardation of reaction velocity ("steric hinc rance"), this process did not prove satisfactory in the hands c the present authors for converting *o*-methylbenzonitrile into *o*-tolu aldehyde, and it has not been possible to include any measurement on the cyanohydrin equilibrium in the case of the latter compounc

The original sample of *cyclo*pentanone was made from adipic aci by the method described in D.R.-P. 256,622; that of *cyclo*hexanon was purchased from Poulenc Frères. The methyl*cyclo*hexanone were made by catalytic reduction of pure cresols supplied by th Graesser Monsanto Co. The *cyclo*heptanone used was a specime of this costly product kindly presented by Professor J. F. Thorpe it was subsequently twice redistilled, small initial and final fractior being rejected as usual.

The following compounds were made in accordance with th authorities quoted: α-Ketotetrahydronaphthalene (Ingold an Piggot, J., 1923, **123**, 1483; compare also Kipping and Hill, J 1899, **75**, 148). xanthrone (Perkin, *Ber.*, 1883, **16**, 339), and anthron (Barnett and Cook, J., 1921, **119**, 904). In other cases the product were prepared by methods in general use.

Method of Determining the Equilibrium Constant.—The solven used throughout was the binary constant-boiling 96% alcohol water mixture, made from the strongest commercial spirit. Th was purified by distillation first from 2% of its weight of oxali acid, then from 5% of sodium hydroxide, and was finally carefull fractionated.

The anhydrous hydrogen cyanide was prepared from potassiun ferrocyanide and dilute sulphuric acid, the vapours being conducte through a series of drying tubes containing calcium chloride liquefied by cooling, and redistilled from phosphoric oxide.

Liquid aldehydes and ketones were weighed by difference fro Lunge pipettes. This had numerous advantages, including ease i manipulation, increased accuracy by reduction of losses due t evaporation and oxidation, and prevention of access of moisture moreover, by counting the drops, a rough control over the quantitie used could be exercised.

A sufficient speed of reaction was ensured by the addition of drop of *n*-tripropylamine, and it was ascertained that variatior in the quantity of this base within limits many times wider tha those which could accidentally be reached in practice had n measurable influence on the state of equilibrium. The equilibriun was finally "frozen," as in the experiments of Ultée and of Jone by addition of excess of nitric acid.

In detail the operations were carried out as follows. A weighe amount of aldehyde or ketone was introduced into a 50 c.c. flas

followed in succession by 30 c.c. of the alcoholic medium and 10 c.c. of the alcoholic hydrogen cyanide.* A very small drop (approximately 0·02 c.c.) of *n*-tripropylamine was added, and the mixture diluted to 50 c.c. with the solvent, confined with a glass stopper, and sealed with paraffin wax. Blank experiments, in which the operations were conducted in exactly the same way but without addition of the aldehyde or ketone, were carried out in each case to determine the total amount of hydrogen cyanide in the system. All solutions were thoroughly mixed, allowed to remain at room temperature over-night, and then kept at 20·0° ± 0·5°, at which temperature any slight contraction, frequently observed after reaction, was corrected, the volumes being made up to the original 50 c.c. by addition of more solvent. Equilibrium in most cases was attained in ½ hour, but this was always checked by comparison with titrations made on the following day.

Among all the cases which the authors have now investigated, that of *o*-nitrobenzaldehyde was the only one in which there was considerable irregularity in the amount of uncombined hydrogen cyanide present after standing for several days, and this was probably due to the extraordinary readiness with which this particular cyanohydrin undergoes complex changes (*Ber.*, 1904, **37**, 948).

The amount of uncombined hydrogen cyanide at equilibrium was determined by withdrawing a measured volume (the amount suitable having been ascertained by a preliminary titration) and adding to it 10 c.c. of *N*/20-silver nitrate solution, acidified with 2 c.c. of concentrated nitric acid in 20 c.c. of water. The precipitated silver cyanide was filtered off, thoroughly washed with water, and the excess of silver in the filtrate and washings determined by titration with *N*/20-potassium thiocyanate, ferric ammonium sulphate being used as indicator in the light given by a Daylight Electric Bulb, with which readings concordant within 0·04 c.c. were easily obtained. Means of two or more results concordant within 0·06 c.c. were used. The blank experiments were completed in the same way.

In all cases the amount of hydrogen cyanide which had combined with the aldehyde or ketone was determined by difference, for although a direct determination of the combined hydrogen cyanide is possible, it involves serious practical difficulties. In the circumstances, the best evidence that no large error was made in the indirect determination is the consistency in the several values for

* The alcoholic hydrogen cyanide was prepared by dissolving 10 c.c. of anhydrous hydrogen cyanide in 250 c.c. of the alcoholic medium; such a solution contained approximately 10 millimols. of HCN in 10 c.c., and remained unaltered in concentration for several weeks when kept in a stoppered glass flask sealed with paraffin wax.

the equilibrium constant calculated from the different determinations in which the relative quantities of reactants at equilibrium varied considerably.

It is evident that errors arising out of inaccurate measurements of the concentrations entering into the formula for the equilibrium constant are proportionately greatest when any of the three concentrations becomes very small, and this tends to be the case if the cyanohydrin has either a very low or a very high dissociation constant, the former being particularly unfavourable for accuracy. These considerations were always kept in mind while deciding the best ranges of concentration and proportions of constituents to be taken in the series of measurements made with each aldehyde and ketone examined.

Errors arising out of temperature variations may be regarded as relatively very small in the case of ketones; Ultée (*Rec. trav. chim.*, 1909, **28**, 281) showed that the increase in dissociation of the cyanohydrins which he used was less than 5% between 0° and 25°, so that even in some exceptional cases during the present series of measurements where the temperature employed was 18°, the difference was not detectable by the methods employed. With aldehyde-cyanohydrins the temperature coefficient is larger. In view of all the circumstances tending to detract from accuracy, the relative values of the functions in the last column in the tables are usually given to two significant figures only.

A serious source of possible error was impurity in the aldehydes and ketones studied, especially when these were liquids. This error as a rule would be largest when the impurity was chemically inert towards the hydrogen cyanide, for example, any residual alcohol used as solvent in the purification process. The presence of another nearly-related aldehyde or ketone (*e.g.*, an isomeride, in comparing constants for monosubstituted benzaldehydes) was less important, and obviously became less serious the more nearly the properties of the impurity approached those of the main constituent.

Example of Procedure and Calculation.—The case of *p*-chlorobenzaldehyde is selected to illustrate how the several independent values of the dissociation constant of each cyanohydrin were determined with various proportions of the interactants in neutral equilibrium. The total amount of the aldehyde or ketone originally taken was different in each determination, so that, although the total concentration of hydrogen cyanide (*i.e.*, free *plus* combined) was the same in each determination, yet the concentrations of both free aldehyde (or ketone) and hydrogen cyanide at equilibrium were different in each case.

In the example which follows, N_A, N_{HCN}, etc., are the numbers of millimols. of reactant per 50 c.c.; N_A refers to the aldehyde (or ketone) originally taken, and N_{HCN}, N_{R_2CO}, and $N_{R_2C(OH)\cdot CN}$ refer respectively to the *free* hydrogen cyanide, free carbonyl compound, and cyanohydrin found at equilibrium. The number of millimols. of *total* hydrogen cyanide, N_T, was taken as the mean of the two values given in the column N_{HCN} for the two blank experiments, *a* and *b*. Thus

$$N_{R_2C(OH)\cdot CN} = N_T - N_{HCN}, \text{ and } N_{R_2CO} = N_A - N_T + N_{HCN}.$$

The values of K given are the equilibrium constants expressed in the usual units, *viz.*, g.-mols. and litres, and are calculated from the arbitrary values, N_{HCN}, etc., by the relation

$$K = C_{HCN} \times C_{R_2CO}/C_{R_2C(OH)\cdot CN} = 2 \times 10^{-2} \times N_{HCN} \times N_{R_2CO}/N_{R_2C(OH)\cdot CN}.$$

The values of ΔF, in g.-calories, are obtained as usual from the relation $\Delta F = 1{\cdot}99 \times 293 \log_e K$ (for K at 293° abs.). Thus ΔF is zero when $K = 1$, *i.e.*, if cyanohydrin, hydrogen cyanide, and aldehyde or ketone are in equilibrium at normal (unit) concentrations; it is positive or negative accordingly as the dissociation constant of the cyanohydrin is greater or less than unity.

p-Chlorobenzaldehyde.

Expt.	N_A.	N_{HCN}.	N_{R_2CO}.	$N_{R_2C(OH)\cdot CN}$.	$K \times 10^3$.
a	0	8·88	0	0	—
b	0	8·87	0	0	—
1	9·02	1·33	1·47	7·55	5·18
2	9·35	1·18	1·65	7·70	5·06
3	10·40	0·83	2·35	8·05	4·84
4	10·68	0·75	2·55	8·13	4·78
5	11·21	0·66	2·99	8·22	4·80

Mean value of $K = (4{\cdot}94 \pm 0{\cdot}06) \times 10^{-3}$.

The "probable error" or "consistency measure," $\pm 0{\cdot}06 \times 10^{-3}$ (*i.e.*, 1·2% of the mean value), was calculated in the usual way.

Discussion of Results in Table I.

It will be convenient to consider in turn the effects of substituents in the para-, meta-, and ortho-positions.

(1) p-*Substitution*.—When the substituents are arranged in the order of their depressant effects on the affinity of the aldehyde for hydrogen cyanide, beginning with the most effective, the list runs:

Substituent	NMe_2	OH	OCH_3	NO_2	CH_3	Cl and H
$\Delta F \times 10^{-2}$	−5·5	−15·0	−20·0	−23·0	−27·0	−31·0

It will be observed that on this basis the three substituents, NMe_2, OH, and OCH_3, which are characterised by their very large

TABLE I.

Constants of Cyanohydrins of some Aromatic Aldehydes.

Benzaldehyde.	No. of deter-*minations.*	$K \times 10^2$.	% Error.	$\Delta F \times 10^{-2}$.
Unsubstituted	4	0·472	0·9	−31
o-Nitro- (m. p. 46°)	6	*ca.* 0·070	5·0	−42
m- „ (m. p. 58°)	5	0·274	2·2	−34
p- „ (m. p. 107°)	4	1·81	3·6	−23
o-Chloro-	5	0·0962	3·4	−40
m- „ (m. p. 17°)	5	0·250	4·0	−35
p- „ (m. p. 47°)	5	0·494	1·2	−31
o-Methoxy- (*m. p.* 35°)	6	0·259	3·9	−35
m- „	4	0·428	2·4	−32
p- „	4	3·12	0·6	−20
o-Hydroxy-	3	1·67	4·4	−24
m- „ (*m. p.* 104°)	4	0·476	0·9	−31
p- „ (m. p. 116°)	3	7·66	0·9	−15
m-Methyl-	5	0·604	2·3	−30
p- „	3	1·03	1·0	−27
2-Methyl-4-methoxy-	4	2·00	3·7	−23
3- „ „	4	3·82	1·0	−19
p-Dimethylamino- (m. p. 73°)	4	39·0	1·1	− 5·5

" *quantitative* " *effects, come first and in their usual order; Cl,* however, with its large electropolar effect, takes a position indicating that the effects produced by its quantitative and electropolar factors just balance one another. The authors' views on the appearance of the nitro-group in quite unusual company have already been stated (pp. 2535, 2538).

(2) m-*Substitution.*—Here the sequence among the substituents examined is:

Substituent	CH_3	HO and H	OCH_3	NO_2	Cl
$\Delta F \times 10^{-2}$	*−30·0*	*−31·0*	*−32·0*	*−34·0*	*−35·0*

This order bears apparently no relation whatever to the quantitative sequence, but definitely indicates that the electropolar effect is the dominant one. Even the methyl group takes its correct position with respect to hydrogen, although the authors admit that this may be fortuitous, for in this relation, as with that of OCH_3 to H, the difference is approaching the probable limits of experimental error. The order of NO_2 and Cl suggests that possibly NO_2, even in the meta-position, increases the extent of non-polar conjugation (Thiele effect) *between the carbonyl group and the nucleus.*

It seems highly significant that if the value of the expression $10^{-2} \times (\Delta F_{para} - \Delta F_{meta})$, that is, of $10^{-2} \times (RT \log_e K_{para} - RT \log_e K_{meta})$, be calculated for any of the single-bonded sub-

stituents measured both in para- and in meta-positions, the results obtained are as follows :

Substituent	OH	OCH_3	Cl	CH_3	H
Difference	+16	+12	+4	+3	±0

The agreement with Flürscheim's quantitative sequence (J., 1909, 95, 726) is remarkable, in spite of the opposite and very widely different electropolar factors of Cl and CH_3. The coincidence cannot fail to suggest that the electropolar effects produced by the substituents are nearly the same at the meta- as at the para-position. If this indeed be so, separation of the qnantitative and electropolar factors is greatly simplified.

(3) o-*Substitution*.—The sequence now is :

Substituent	OH	H	OCH_3	Cl	NO_2
$\Delta F \times 10^{-2}$	−24·0	−31·0	−35·0	−40·0	−42·0

The position of OH in this list is almost certainly attributable, not to its quantitative factor, but to the circumstance that *o*-hydroxybenzaldehyde is not comparable with other substituted benzaldehydes, the true hydroxy-compound existing largely as a more stable form where there is chelation between the bydroxyl and carbonyl groups, as Sidgwick and his co-workers have shown (J., 1924, **125**, 527; 1925, **127**, 907). Such an occurrence as this must have the effect of reducing the apparent stability of the cyanohydrin. The other groups, OCH_3, Cl, and NO_2, when in the ortho-position all act so as to increase the stability of the cyanohydrin relatively to that of the aldehyde. In view of the opposite effect which OCH_3 exercises when in the para-position, the large gap between the values of ΔF for ortho-situated OCH_3 and Cl may well be due to the opposite signs of the quantitative factors of these two substituents.

o-Methylbenzaldehyde could not be obtained for examination, but comparison of the numbers found for 2- and for 3-methyl-4-methoxybenzaldehyde show that in the ortho-position, CH_3, like OCH_3, Cl, and NO_2, raises the stability of the cyanohydrin in comparison with that of the aldehyde.

Discussion of Results in Table II.

Here are given a number of dissociation constants for cyanohydrins of cyclic ketones and (in parentheses) of some corresponding open-chain compounds. The effect of ring formation may be roughly shown by subtracting from the value of ΔF for the cyclic ketone that for its open-chain analogue. In the following list the name of the former only is given and the numbers represent the gains

TABLE II.

Constants of Cyanohydrins of some Cyclic (and Related) Ketones.

Ketone.	No. of determinations.	$K \times 10^2$.	% Error.	$\Delta F \times 10^{-2}$.
*cyclo*Pentanone	4	1·49	2·8	−24
(Methyl *n*-propyl ketone)... ..	4	3·54	2·3	−19
*cyclo*Hexanone	4	0·092	4·3	−41
(Methyl *n*-butyl ketone)	4	3·22	1·2	−20
2-Methyl*cyclo*hexanone.........	5	0·059	5·4	−43
3- ,, ,, ,, ...	4	0·30	1·1	−34
4- ,, ,, ,, ...	4	0·127	2·0	−39
Menthone	4	6·54	1·8	−16
*cyclo*Heptanone	4	7·96	1·0	−15
Camphor	(No appreciable cyanohydrin formation.)			>> +10
α-Hydrindone	3	610·0	9·0	+11
(Phenyl ethyl ketone)	5	59·4	1·7	− 3
α-Ketotetrahydronaphthalene	3	806·0	10·0	+10·2
(Phenyl *n*-propyl ketone)......	5	89·4	1·2	− 0·65
Fluorenone	3	146·0	0·6	+ 2·3
(Benzophenone)	(*No appreciable* cyanohydrin formation.)			>> +10
Anthrone and *Xanthrone*	(*No appreciable* cyanohydrin formation.)			>> +10

in the free energy of dissociation ($\Delta F \times 10^{-2}$) consequent upon ring closure :

*cyclo*Pentanone	−5·0	α-Hydrindone	+13·5
*cyclo*Hexanone	−20·7	α-Ketotetrahydronaphthalene	+10·9
*cyclo*Heptanone	+*ca.* 6·5	*Fluorenone ... very large and negative*	

In some cases, then, and more especially in those of *cyclo*hexanone and fluorenone, ring formation in effect greatly increases the stability of the addition compound, and, with *cyclo*hexanone and its methyl derivatives, the result is to render the corresponding ketone-cyanohydrins the most stable known. In some cases, on the other hand, ring formation has the opposite result, and this is especially remarkable in the case of α-hydrindone, where ortho-snbstitution such as is involved in the ring formation would ordinarily tend to *stabilise the cyanohydrin.*

The effects of introducing methyl groups into *cyclo*hexanone have the appearance of an induced alternate effect, but this can scarcely be more than a coincidence. It seems much more probable that the normal electron-releasing electropolar effect of methyl is larger in the 3- than in the 4-position, whilst in the 2-methyl derivative an electron-restraining effect (similar to that produced by ortho-situated methyl in aromatic acids and aldehydes) enters, dominating all others.

The very large depressant effect of the *iso*propyl group in position 2- in 3-methyl-2-*iso*propylhexanone (menthone) is most striking, for methyl in that position has the opposite effect. Possibly this may be a true case of interference by configurational strain in the

cyanohydrin due to crowding. It has always appeared probable that the so-called steric effects are associated with, and therefore conditioned by, the amount of branching of chains.

Summary.

The constants for the dissociation

$$R^1 \cdot C(OH)(CN) \cdot R^2 \longleftrightarrow R^1 \cdot CO \cdot R^2 + HCN$$

of a number of cyanohydrins derived from aldehydes and ketones have been determined in 96% alcohol at $20° \pm 0{\cdot}5°$.

The dissociation constants of cyanohydrins derived from benzaldehyde and its substitution derivatives appear to be affected by the same factors which influence the ionisation constants of benzoic acid and its substitution derivatives (Flürscheim, J., 1909, **95**, 726), although (i) the "electropolar" factor appears to be of relatively less importance in the para-substituted cyanohydrins, and (ii) the "quantitative" factor has little if any influence in the meta-substituted cyanohydrins. The effects of ortho-substituents examined (other than HO) are such as to depress the dissociation constants of the cyanohydrin, and this is in direct contrast to the result to be anticipated from the classical "space-occupation" hypothesis so frequently used to account for other effects associated with ortho-substitution. Ring closure (with elimination of two atoms of hydrogen) in a chain comprising a carbonyl carbon atom leads sometimes to a large increase and sometimes to a large decrease in the dissociation constant of the derived cyanohydrin.

The results obtained are discussed from the point of view of the electronic theory, and it is suggested that possibly the additive capacity of carbonyl carbon and ethylenic carbon, considered from the standpoint of entropy, does not increase continuously with the restraint on its electrons but reaches a maximum and then declines, just as in the series, boron, carbon, nitrogen, and oxygen, the capacity to form stable compounds, in which the element exercises a co-ordination number of 4, attains a maximum at carbon.

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CCCXXXVII.—*A New Reaction of Certain Diazo-sulphonates derived from β-Naphthol-1-sulphonic Acid. Part II. The Constitution of Nitro- and Amino-phenylphthalazones.*

By FREDERICK MAURICE ROWE and ESTHER LEVIN.

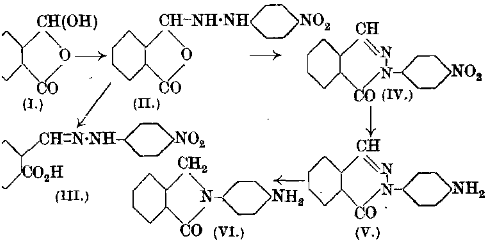
IN a former communication (J., 1926, 700) we stated that 1-hydroxy-3-(4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid (VII) is reprecipitated unaltered by diluting a solution in cold concentrated sulphuric acid, but boiling with aqueous sulphuric acid gives a substance which is not precipitated from the solution on further dilution. The latter substance has now been examined more closely. Acetic acid is eliminated during the reaction, and analysis of the product, yellow needles, m. p. 333°, gave the formula $C_{14}H_9O_3N_3$, which is that of a nitrophenylphthalazone. Consequently, this reaction is analogous to the conversion of 1-hydroxy-3-(4′-aminophenyl)-tetrahydrophthalazine-4-acetic acid (VIII) into an aminophenylphthalazone by boiling with aqueous mineral acid (*loc. cit.*, p. 703). The product obtained by the reduction of the nitrophenylphthalazone varies with the conditions used. Thus, reduction with aqueous sodium sulphide gives the aminophenylphthalazone, which we described previously as 4′-amino-3-phenylphthalaz-4-one, whereas zinc dust and hydrochloric acid give 4′-amino-*N*-phenylphthalimidine.

Seekles (*Rec. trav. chim.*, 1924, **43**, 329) has described as a nitrophenylphthalazone a substance, deep orange needles, becoming paler at 228° and melting at 259°, which he obtained by condensing *o*-phthalaldehydic acid with *p*-nitrophenylhydrazine in alcoholic solution. This compound obviously is not identical with ours, and its method of preparation should lead to 4′-nitro-3-phenylphthalaz-4-one. If that is the case, our compound is the isomeric *4′-nitro-3-phenylphthalaz-1-one* (IX), and the compound which we described previously as 4′-amino-3-phenylphthalaz-4-one is actually *4′-amino-3-phenylphthalaz-1-one* (X). Consequently, in converting 1-hydroxy-3-(4′-aminophenyl)tetrahydrophthalazine-4-acetic acid into the aminophenylphthalazone with elimination of acetic acid, it is not the $>CH{\cdot}CH_2{\cdot}CO_2H$ group, but the $>CH{\cdot}OH$ group, which is converted into a keto-group.

Unsuccessful attempts were made to confirm this hypothesis by eliminating the amino-group from our aminophenylphthalazone, so that the corresponding phenylphthalazone could be compared with 3-phenylphthalaz-4-one (Racine, *Annalen*, 1887, **239**, 86; Thiele and Falk, *ibid.*, 1906, **347**, 112), of which the constitution is

efinitely known. Diazotisation and boiling with alcohol under a ariety of conditions, or diazotisation, and reduction of the diazo-ium compound to the hydrazine, followed by oxidation with opper acetate, gave no phenylphthalazone. In the latter case, isruption of the molecule undoubtedly occurred.

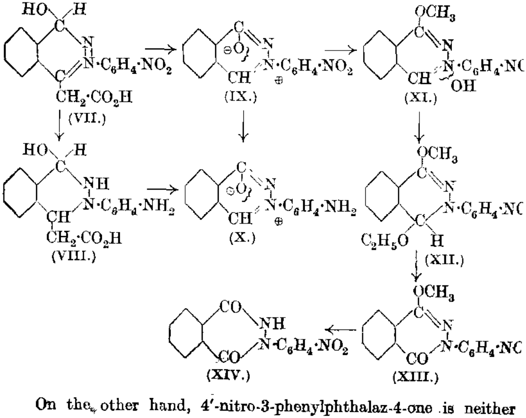
It appeared desirable, therefore, to prepare Seekles's compound or purposes of comparison, and, as a result, it was found not to be a itrophenylphthalazone. The condensation of an equimolecular roportion of phthalaldehydic acid and *p*-nitrophenylhydrazine in oiling alcoholic solution gives the compound described by Seekles, ut it has the formula $C_{14}H_{11}O_4N_3$ and is actually only an inter-iediate stage in the formation of the nitrophenylphthalazone. In coholic solution, phthalaldehydic acid reacts mainly in the ıutomeric form of hydroxyphthalide (I), and under these conditions ondensation is limited to formation of the lactone form of *o-carboxy-nzaldehyde-*p*-nitrophenylhydrazone* (II), which Seekles described s a nitrophenylphthalazone. This condensation product dissolves ı sodium carbonate owing to conversion into the free *acid* (III), ut on boiling a nitrobenzene solution a molecule of water is iminated and gives the actual *4′-nitro-3-phenylphthalaz-4-one* (IV), olourless needles, m. p. 258°, which is isomeric and not identical ith the nitrophenylphthalazone we have obtained from 1-hydroxy-·(4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid.



4′-Nitro-3-phenylphthalaz-4-one, although sparingly soluble in ineral acids, does not form salts with them and is insoluble in dium hydroxide. Reduction with sodium sulphide gives the tual *4′-amino-3-phenylphthalaz-4-one* (V), and reduction with zinc ıst and hydrochloric acid gives 4-′amino-*N*-phenylphthalimidine 'I), *but the conversion into the latter does not proceed so readily* in the case of 4′-nitro-3-phenylphthalaz-1-one.

The formula (IX) for *4′-nitro-3-phenylphthalaz-1-one* appears to

agree best with its properties. Thus, it is acidic and dissolves readily in sodium hydroxide with a bluish-red colour; also it is basic and dissolves readily in mineral acids, forming well-crystallised salts, decomposed by water; and it forms a *picrate*. Further, it would be anticipated that the oxygen atom of the keto-group in a compound of this constitution could be methylated, and this proved to be the case, although the course of the reaction was somewhat complicated. The product of the interaction of 4′-nitro-3-phenylphthalaz-1-one with methyl sulphate in nitrobenzene solution, after removal of the latter, is obtained as an aqueous solution of the *methosulphate*, and is isolated as an orange-yellow, amorphous powder by making alkaline with sodium carbonate. This *substance*, probably (XI), crystallises well from alcohol, but it combines with the alcohol, probably forming (XII), and is then so reactive that it was impossible to determine its formula analytically. This proved to be immaterial, however, for by heating the compound after crystallisation from alcohol first at 110° and then at 140° it is readily converted into 4-*keto*-1-*methoxy*-3-(4′-*nitrophenyl*)-3 : 4-*dihydrophthalazine* (XIII), which is neither acidic nor basic. This compound is demethylated by heating with hydrobromic acid and glacial acetic acid in a sealed tube at 100° with formation of 1 : 4-*diketo*-3-(4′-*nitrophenyl*)*tetrahydrophthalazine* (XIV).



On the other hand, 4′-nitro-3-phenylphthalaz-4-one is neither

acidic nor basic, it does not form a picrate, and is unaltered by treatment with methyl sulphate under conditions identical with those used in the case of 4′-nitro-3-phenylphthalaz-1-one.

EXPERIMENTAL.

4′-Nitro-3-phenylphthalaz-1-one (IX).—A mixture of 10 g. of finely-powdered 1-hydroxy-3-(4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid (VII), 50 c.c. of concentrated sulphuric acid, and 60 c.c. of water was boiled (b. p. 140°) under reflux. Solution was complete after ½ hour, and boiling was continued for a further 1½ hours, acetic acid being eliminated during the reaction. The mixture was cooled, diluted with 240 c.c. of water, boiled, and filtered. After cooling, the sulphate, colourless needles, was filtered off and neutralised with sodium carbonate. A further quantity, but less pure, was isolated by neutralising the filtrate. The united product was purified through the sparingly soluble hydrochloride, long, colourless needles, and, after neutralisation with sodium carbonate, the *base* crystallised from pyridine in fine yellow needles, m. p. 333° (not 331° as previously given) (yield 5·6 g.; 68·5%) (Found: C, 62·9; H, 3·5; N, 15·7. $C_{14}H_9O_3N_3$ requires C, 62·9; H, 3·4; N, 15·7%). The substance is readily soluble in glacial acetic acid, soluble in nitrobenzene, sparingly soluble in alcohol and ethyl acetate, and very sparingly soluble in benzene. It is insoluble in sodium carbonate, but dissolves in sodium hydroxide with a bluish-red colour, changing to orange-brown on keeping; with mineral acids it forms salts which are readily decomposed by water. With an alcoholic solution of picric acid it forms a *picrate*, fine bright yellow needles, m. p. 218°, which appear to be decomposed progressively by recrystallisation from alcohol (Found: C, 48·6; H, 2·5. $C_{20}H_{12}O_{10}N_6$ requires C, 48·4; H, 2·4%).

Reduction of 4′-Nitro-3-phenylphthalaz-1-one.—(*a*) A fine suspension of 2 g. of 4′-nitro-3-phenylphthalaz-1-one in 50 c.c. of water was heated to 50° with a solution of 16 g. of sodium sulphide crystals in 15 c.c. of water. The bluish-red colour of the solution changed to reddish-orange, and orange-coloured needles separated. The mixture was then boiled for 10 minutes, cooled, and filtered. The *4′-amino-3-phenylphthalaz-1-one* (X) crystallised from alcohol in deep straw-coloured, prismatic needles, m. p. 259° (yield 1 g.; 56%), and is identical with the compound which we described formerly as 4′-amino-3-phenylphthalaz-4-one. (*b*) A solution of 2 g. of 4′-nitro-3-phenylphthalaz-1-one in 50 c.c. of water and 75 c.c. of concentrated hydrochloric acid was boiled, and 4 g. of zinc dust were added gradually with vigorous boiling. The 4′-amino-N-phenylphthalimidine (VI), almost colourless, prismatic needles,

m. p. 198° (yield 1·3 g.; 77%), was isolated as previously describ (*loc. cit.*, p. 704).

Action of Methyl Sulphate on 4'-Nitro-3-phenylphthalaz-1-one.— solution of 5 g. of 4'-nitro-3-phenylphthalaz-1-one in 120 c.c. boiling, dry nitrobenzene was cooled to about 140°, and 2·5 g. methyl sulphate were added to the crystalline mixture. T crystals disappeared rapidly and the reaction was completed l heating uuder reflux at 150° for ½ hour. Nitrobenzene was remov by distillation with steam, and the aqueous residue, after filtering fro a little resin, gave an orange-yellow, flocculent precipitate wh rendered alkaline with sodium carbonate. This *substance* (X forms a hydrochloride, stout colourless needles, and is unaltered l prolonged boiling with hydrochloric acid; it is insoluble in co alkalis, but is decomposed by boiling with sodium hydroxide. C addition of alcohol to the dry compound, it became resinous and th crystalline, and after crystallising four times from ethyl alcoh formed large, orange, elongated, hexagonal prisms (XII), m. 138—141° (Found: C, 63·3; H, 5·7; N, 13·6; total OR, calculate as OMe, 18·3%). On the other hand, crystallisation from meth alcohol gave orange leaflets and diamond-shaped crystals, m. 173—175° (Found: C, 62·3; H, 5·1; OMe, 18·5%). No definit conclusions as to the composition of these compounds after crystalli ation from methyl or ethyl alcohol could be based on these analyse however, because the substance has combined with the alcohols an the products are decomposed partially even by drying in a vacuu at the ordinary temperature, as was done for the preparation of th analytical specimens, whilst at 100° the crystals become opaque an are converted gradually into 4-keto-1-methoxy-3-(4'-nitrophenyl 3:4-dihydrophthalazine (XIII). The latter change was bes effected by heating first at 100° and then at 140°.

4-*Keto*-1-*methoxy*-3-(4'-*nitrophenyl*)-3:4-*dihydrophthalazine* crysta lised from alcohol in fine pale yellow needles, or from glacial acet acid in colourless needles, m. p. 199° (Found: C, 60·9; H, 3·9 N, 14·3; OMe, 10·3. $C_{15}H_{11}O_4N_3$ requires C, 60·6; H, 3·7; N 14·1; OMe, 10·4%). The substance is readily soluble in chloroform ethyl acetate and toluene, but insoluble in dilute mineral acids c alkalis. When 1 g. was heated with glacial acetic acid and twice th volume of hydrobromic acid in a sealed tube at 100° for abou 10 minutes, 1:4-*diketo*-3-(4'-*nitrophenyl*)*tetrahydrophthalazine* (XIV separated, and after recrystallisation from glacial acetic aci formed colourless needles, m. p. 307° (Found: C, 59·5; H, 3·4 N, 15·0. $C_{14}H_9O_4N_3$ requires C, 59·4; H, 3·2; N, 14·8%), insolubl in dilute mineral acids, but soluble in dilute sodium carbonate giving a pale yellow colour.

4'-Nitro-3-phenylphthalaz-4-one (IV).—A mixture of a solution of 4·5 g. of *o*-phthalaldehydic acid in 100 c.c. of alcohol and a solution of 4·6 g. of *p*-nitrophenylhydrazine in 80 c.c. of alcohol was boiled under reflux for about 5 minutes after the lactone form of o-*carboxybenzaldehyde*-p-*nitrophenylhydrazone* (II) had separated in orange needles, m. p. 254° after shrinking and becoming paler at 228° (Found: C, 58·6; H, 4·0; N, 14·9. $C_{14}H_{11}O_4N_3$ requires C, 58·9; H, 3·9; N, 14·7%). It is sparingly soluble in dilute hydrochloric acid and soluble in dilute sodium carbonate owing to opening of the ring with formation of o-*carboxybenzaldehyde*-p-*nitrophenylhydrazone* (III), which is precipitated on acidifying the alkaline solution as a red powder, decomposing at 218° and then melting at 249°. Attempts to recrystallise the lactone form from alcohol or pyridine resulted in its conversion into *4'-nitro-3-phenylphthalaz-4-one*. The latter compound was prepared most conveniently by boiling a nitrobenzene solution for a short time; after cooling, it crystallised in long, colourless, glistening needles, m. p. 258° (Found: C, 63·0; H, 3·4; N, 15·7. $C_{14}H_9O_3N_3$ requires C, 62·9; H, 3·4; N, 15·7%). It is almost insoluble in alcohol, insoluble in sodium carbonate or hydroxide, but very sparingly soluble in hydrochloric acid. It neither forms a picrate nor reacts with methyl sulphate.

4'-Amino-3-phenylphthalaz-4-one (V).—A fine suspension of 2 g. of the lactone in 50 c.c. of water was heated to 50° with a solution of 16 g. of sodium sulphide crystals in 15 c.c. of water. The bluish-red colour of the solution changed to orange-yellow, and on further heating, almost colourless crystals separated in small yield. The *4'-amino-3-phenylphthalaz-4-one* crystallised from alcohol or water in long, pale yellow needles, m. p. 184° (Found: C, 70·7; H, 4·7; N, 17·9. $C_{14}H_{11}ON_3$ requires C, 70·9; H, 4·6; N, 17·7%). It is soluble in hot water, insoluble in alkalis, but soluble in dilute acids (*hydrochloride*, colourless needles), and can be diazotised. A solution of 1 g. in 10 c.c. of glacial acetic acid was boiled with 0·2 c.c. of acetic anhydride for 2 hours and poured into water; the *acetyl* derivative crystallised from dilute alcohol in colourless, feathery needles, m. p. 233° (Found: N, 15·0. $C_{16}H_{13}O_2N_3$ requires N, 15·0%). Reduction of the lactone form with zinc dust and hydrochloric acid, as described on p. 2553, resulted also in the formation of 4'-amino-*N*-phenylphthalimidine (VI), almost colourless needles, m. p. 198°, although with greater difficulty and in much lower yield.

We desire to thank Professor Robert Robinson, F.R.S., for his continued interest in this series of investigations.

LEEDS UNIVERSITY. [*Received, June 26th*, 1928.]

CCCXXXVIII.—*A New Reaction of Certain Diaz sulphonates derived from β-Naphthol-1-sulphon Acid. Part III. Preparation of Phthalazin Phthalazone, and Phthalimidine Derivatives fro m-Nitroaniline.*

By FREDERICK MAURICE ROWE, MAHMED AHMED HIMMAT, and ESTHER LEVIN.

IN Parts I and II of this series (J., 1926, 690: preceding pape the preparation of phthalazine, phthalazone, and phthalimidi derivatives from 4′-nitrobenzene-2-naphthol-1-diazosulphonate h been described, and the constitution of the isomeric 4′-nitro- a -amino-phenylphthalazones discussed. The investigation has no been extended to the corresponding 3′-nitro- and amino-derivative

3′-Nitrobenzene-2-naphthol-1-diazosulphonate is formed quanti atively from diazotised *m*-nitroaniline and β-naphthol-1-sulphon acid in acid solution, but conversion through *sodium* 1-3′-*nitr benzeneazo*-β-*naphthaquinone*-1-*sulphonate* into *sodium hydrog* 3-(3′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic acid*-1-*sulphona* is accompanied by no marked change in colour and does not pr ceed so readily as in the case of the 4′-nitro-isomeride, owing to a increased tendency to the formation of 3′-nitrobenzeneazo-β naphthol in appreciable quantities. This side reaction is limite by working at greater dilution, but under the best conditions th yield is 15% less than that obtained with the 4′-nitro-isomerid Monosodium 3-(3′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acet acid-1-sulphonate resembles the 4′-nitro-isomeride in general prope ties, although it is noteworthy that, whereas the latter is a leve dyeing, pure greenish-yellow, acid dye of good tinctorial powe the former possesses hardly any tinctorial properties. Th replacement of the sodium-1-sulphonate group by hydroxyl give 1-*hydroxy*-3-(3′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic acid* in yield of about 10% less than was obtained with the 4′-nitro-isomerid *Esters* and an *anilide* of this hydroxy-compound were obtaine readily, but attempts to prepare an acetyl derivative failed, fo although a variety of conditions was employed the product wa always resinous and could not be crystallised. Unlike the 4′-nitr isomeride, 1-hydroxy-3-(3′-nitrophenyl)-1 : 3-dihydrophthalazine-4 acetic acid is not reduced satisfactorily by alkaline hydrosulphit [hyposulphite], for the compounds in the present series appear t be more sensitive to alkalis, and although the product resembled tha anticipated in appearance and solubility in acids and alkalis, it coul

not be purified by crystallisation and was not converted into the corresponding aminophenylphthalazone by boiling with mineral acid. 1-*Hydroxy*-3-(3′-*aminophenyl*)*tetrahydrophthalazine*-4-*acetic acid* is obtained satisfactorily, however, by reduction with stannous chloride and hydrochloric acid, because its hydrochloride is so sparingly soluble in concentrated hydrochloric acid that the reaction does not proceed further even after prolonged boiling. On the other hand, by boiling 1-hydroxy-3-(3′-aminophenyl)tetrahydrophthalazine-4-acetic acid with aqueous sulphuric acid (b. p. 140°), acetic acid is eliminated and 3′-*amino*-3-*phenylphthalaz*-1-*one* is obtained in a 91% yield. When this is reduced with zinc dust and hydrochloric acid, one nitrogen atom is eliminated as ammonia and 3′-*amino*-N-*phenylphthalimidine* is produced. The replacement of the amino-group in the latter by hydrogen or by hydroxyl proceeds as with the 4′-amino-isomeride, except that, as the diazonium chloride obtained from 3′-amino-*N*-phenylpbthalimidine is less stable to the action of boiling dilute sulphuric acid, 3′-*hydroxy*-N-*phenylphthalimidine* is formed with greater ease.

When 1-hydroxy-3-(3′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid is boiled with sulphuric acid (b. p. 140°), it loses acetic acid and 3′-*nitro*-3-*phenylphthalaz*-1-*one* is formed, but in a yield of 12% less than was obtained with the 4′-nitro-isomeride. 3′-Nitro-3-phenylphthalaz-1-one is much less acidic than the latter, but with mineral acids it also forms well-crystallised salts, decomposed by water, and it forms a more stable *picrate*. The product obtained from it by reduction varies with the conditions used. Thus, reduction with aqueous sodium sulphide gives 3′-amino-3-phenylphthalaz-1-one, although in a yield of 17% less than was obtained by the action of aqueous sulphuric acid on 1-hydroxy-3-(3′-aminophenyl)tetrahydrophthalazine-4-acetic acid, whereas zinc dust and hydrochloric acid give 3′-amino-*N*-phenylphthalimidine. 3′-Nitro-3-phenylphthalaz-1-one reacts with methyl sulphate in a similar manner to the 4′-nitro-isomeride, and the primary product behaves similarly with methyl or ethyl alcohol. After crystallisation from alcohol, heating gives 4-*keto*-1-*methoxy*-3-(3′-*nitrophenyl*)-3 : 4-*dihydrophthalazine*, but this is always accompanied by a more complex substance, especially if heating is too rapid at first. 1 : 4-*Diketo*-3-(3′-*nitrophenyl*)*tetrahydrophthalazine* is obtained from the methoxy-compound by the action of hydrobromic acid.

Finally, 3′-*nitro*-3-*phenylphthalaz*-4-*one* was prepared for purposes of comparison. The condensation of equimolecular proportions of phthalaldehydic acid and *m*-nitrophenylhydrazine in boiling alcoholic solution gives the *lactone* form of the *m*-nitrophenylhydrazone, and when a nitrobenzene solution of this is boiled, a molecule of water is

eliminated with formation of 3′-nitro-3-phenylphthalaz-4-one. The latter, although very sparingly soluble in mineral acids, does not form salts either with them or with picric acid, is insoluble in sodium hydroxide, and is unaltered by treatment with methyl sulphate under conditions identical with those used in the case of 3′-nitro-3-phenylphthalaz-1-one.

The lactone form of *o*-carboxybenzaldehyde-*p*-nitrophenylhydrazone is converted into 4′-amino-3-phenylphthalaz-4-one by treatment with warm aqueous sodium sulphide, but the corresponding *m*-nitro-derivative is merely converted into 3′-nitro-3-phenylphthalaz-4-one, which separates and remains unaltered even after prolonged boiling. *3′-Amino-3-phenylphthalaz-4-one*, however, is readily obtained by reducing 3′-nitro-3-phenylphthalaz-4-one with alkaline hydrosulphite.

Further work on this subject is in progress.

Experimental.

Sodium Hydrogen 3-(3′-Nitrophenyl)-1 : 3-dihydrophthalazine-4-acetate-1-sulphonate.—A filtered solution of 50 g. of commercial sodium β-naphthol-1-sulphonate in 220 c.c. of water was stirred into a cold solution of diazotised *m*-nitroaniline, obtained by adding a concentrated solution of 14 g. of sodium nitrite to a solution of 24 g. of *m*-nitroaniline in 60 c.c. of concentrated hydrochloric acid and 180 c.c. of water. The 3′-nitrobenzene-2-naphthol-1-diazosulphonate separated immediately as a yellowish-brown precipitate in theoretical yield (calculated on the *m*-nitroaniline). This was filtered off, washed free from acid with brine, made into a paste with 600 c.c. of cold water, and a cold solution of 50 g. of anhydrous sodium carbonate in 250 c.c. of water was added. The *sodium 1-3′-nitrobenzeneazo-β-naphthaquinone-1-sulphonate* formed does not separate from the solution at this dilution. The cold, clear, yellowish-brown solution was added immediately to a cold solution of 60 g. of sodium hydroxide in 120 c.c. of water, the temperature rose about 10°, and the deep reddish-brown mixture was left overnight. Conversion into sodium 3-(3′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid-1-sulphonate was accompanied by little change in colour. The mixture was rendered faintly acid with hydrochloric acid, then made alkaline with sodium carbonate, and a small amount of 3′-nitrobenzeneazo-β-naphthol (Metanitraniline Orange) filtered off. The latter should not be washed with hot water, as this renders the product resinous and difficult to coagulate. The filtrate was rendered faintly acid with hydrochloric acid, and salt added cautiously until the monosodium salt of the product separated completely as a yellowish-brown, semi-crystalline precipitate.

After drying, the product was separated from sodium chloride by extraction with absolute alcohol, from which it crystallised in orange-yellow prisms (yield 55 g.; 76·3%) (Found: S, 7·7. $C_{16}H_{12}O_7N_3SNa$ requires S, 7·7%). It is readily soluble in water, but less soluble in alcohol, forming yellow solutions, which are deepened in colour by the addition of alkalis. The aqueous solution is decolorised by zinc dust and ammonia, and on exposure to air a deeper colour returns. Unlike tbe 4′-nitro-isomeride (J., 1926, 699), it possesses but little tinctorial power.

1-Hydroxy-3-(3′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic Acid.—An aqueous solution of monosodium-3-(3′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid-1-sulphonate (32 g.) was boiled with concentrated hydrochloric acid (aqueous sulphuric acid also can be used) as described for the 4′-nitro-isomeride (*ibid.*, p. 700). The product crystallised from ethyl acetate in pale yellow, prismatic needles, m. p. 234° (yield 21·3 g.; 83·5%) (Found: C, 58·9; H, 4·0; N, 12·9. $C_{16}H_{13}O_5N_3$ requires C, 58·7; H, 4·0; N, 12·8%). The substance is readily soluble in alcohol or glacial acetic acid, but less soluble in benzene, acetone, or etber. It is sparingly soluble in water, forming a solution acid to litmus, but dissolves readily in sodium carbonate with an orange-yellow colour, or in sodium hydroxide with a deep reddish-brown colour. It dissolves in cold concentrated sulphuric acid with a yellow colour and is reprecipitated unaltered on dilution, but when boiled with aqueous sulphuric acid it is converted into 3′-nitro-3-phenylphthalaz-1-one.

Derivatives of 1-Hydroxy-3-(3′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic Acid.—The *methyl* ester, prepared as described for the 4′-nitro-isomeride (*ibid.*, p. 700), crystallised from methyl alcohol in pale yellow needles, m. p. 184° (Found: C, 59·7; H, 4·5; N, 12·2. $C_{17}H_{15}O_5N_3$ requires C, 59·8; H, 4·4; N, 12·3%). The *ethyl* ester, similarly prepared, crystallised from ethyl alcohol in pale yellow needles, m. p. 195° (Found: C, 61·1; H, 5·0; N, 11·9. $C_{18}H_{17}O_5N_3$ requires C, 60·8; H, 4·8; N, 11·8%). It is insoluble in sodium carbonate, but dissolves in sodium hydroxide with a reddish-brown colour. The *anilide* was prepared as described for the 4′-nitro-isomeride and, after several crystallisations from ethyl acetate, formed transparent, yellow prisms, m. p. 239° (decomp.) (Found: C, 65·8; H, 4·8; N, 13·9. $C_{22}H_{18}O_4N_4$ requires C, 65·7; H, 4·5; N, 13·9%). It is almost insoluble in cold sodium hydroxide, whereas the 4′-nitro-isomeride is readily soluble with a red colour, and it is also hydrolysed to the original acid by boiling concentrated hydrochloric acid.

1-Hydroxy-3-(3′-aminophenyl)tetrahydrophthalazine-4-acetic Acid.—1-Hydroxy-3-(3′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid

(20 g.) was boiled under reflux with a solution of stannous chlorid (80 g.) in concentrated hydrochloric acid (200 c.c.) until it had al dissolved and been replaced by the hydrochloride of 1-hydroxy-3 (3′-aminophenyl)tetrahydrophthalazine-4-acetic acid, colourles cubic crystals. After a further 10 minutes' boiling, the hydrochlorid was filtered off, washed with cold concentrated hydrochloric acid and dissolved in water; tin was removed from the solution by means of hydrogen sulphide, and the product isolated by addin sodium carbonate until a white precipitate had separated completely After being washed with cold water, it crystallised from boiling wate in almost colourless, glistening prisms, m. p. 252° (yield 15·7 g. 86%) (Found: C, 64·4; H, 5·4; N, 14·2. $C_{16}H_{17}O_3N_3$ require C, 64·2; H, 5·7; N, 14·0%). This compound cannot be obtaine satisfactorily by reduction with alkaline hydrosulphite. It is sparingly soluble in alcohol and benzene, more soluble in water than th 4′-amino-isomeride, and, unlike the latter, gives no coloration wit ferric chloride. It dissolves readily in dilute alkalis or dilute acids and can be diazotised. Direct esterification in this case also proved unsatisfactory, but there was no difficulty in preparing a pure *acetyl* derivative, which crystallised from boiling water in colourless prisms, m. p. 167° (Found: C, 63·5; H, 5·5; N, 12·1. $C_{18}H_{19}O_4N_3$ requires C, 63·3; H, 5·6; N, 12·3%).

3′-*Amino-3-phenylphthalaz-1-one*.—A solution of 5 g. of 1-hydroxy 3-(3′-aminophenyl)tetrahydrophthalazine-4-acetic acid in a mixture of 25 c.c. of concentrated sulphuric acid and 30 c.c. of water was boiled (b. p. 140°) under reflux for 1½ hours, acetic acid being eliminated during the reaction. After cooling, the solution was diluted with 50 c.c. of water, neutralised with sodium hydroxide, then made distinctly alkaline with sodium carbonate and filtered. The base crystallised from alcohol in stout, golden-yellow, spear-shaped prisms, m. p. 210° (yield 3·6 g.; 91%) (Found: C, 71·1; H, 4·8; N, 17·8. $C_{14}H_{11}ON_3$ requires C, 70·9; H, 4·6; N, 17·7%). It is soluble in hot water, sparingly soluble in acetone, and insoluble in benzene. It is insoluble in alkalis, but soluble in dilute acids and can be diazotised; the hydrochloride formed colourless needles, and the *acetyl* derivative crystallised from boiling water in fine, colourless needles, m. p. 204° (Found: C, 68·7; H, 4·9; N, 14·8. $C_{16}H_{13}O_2N_3$ requires C, 68·8; H, 4·7; N, 15·0%).

3′-*Amino*-N-*phenylphthalimidine*.—3′-Amino-3-phenylphthalaz-1-one was reduced with zinc dust and hydrochloric acid as described for the 4′-amino-isomeride (*loc. cit.*). After cooling, the product separated completely as colourless plates of the hydrochloride, together with a small proportion of colourless needles of the *zinc*

ouble chloride; the filtrate contained ammonia. The crystals were issolved in a little hot water and hydrochloric acid, the solution ;as rendered alkaline, and the dry precipitate extracted with lcohol. The base crystallised in almost colourless prismatic eedles, m. p. 175° (Found: C, 75·1; H, 5·7; N, 12·8. $C_{14}H_{12}ON_2$ equires C, 75·0; H, 5·4; N, 12·5%). The *acetyl* derivative crystalsed from alcohol in colourless, silky needles, m. p. 204° (Found: ', 71·9; H, 5·6; N, 10·6. $C_{16}H_{14}O_2N_2$ requires C, 72·2; H, 5·4; ;, 10·5%). *N*-Phenylphthalimidine, almost colourless plates, m. p. 60°, was obtained by diazotising 3'-amino-*N*-phenylphthalimidine ılphate, and boiling the sparingly soluble diazonium sulphate ılmost colourless needles) with alcohol.

3'-Hydroxy-N-phenylphthalimidine.—This compound was prepared 'om 3'-amino-*N*-phenylphthalimidine (10 g.) as described for the '-hydroxy-isomeride (*loc. cit.*, p. 704), except that, as the diazoompound in the present case was less stable, boiling for longer ıan ½ hour was unnecessary. The hydroxy-derivative crystallised 'om alcohol in colourless glistening leaflets, m. p. 268° (yield 9·5 g.; 5%) (Found: C, 75·0; H, 5·0; N, 6·4. $C_{14}H_{11}O_2N$ requires ', 74·7; H, 4·9; N, 6·2%). Its *methyl* ether, m. p. 122° (Found: ', 75·0; H, 5·5; N, 6·0. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·4; [, 5·9%), and *ethyl* ether, m. p. 115° (Found: C, 75·7; H, 5·9; [, 5·6. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·9; N, 5·5%), crystallised 'om the corresponding alcohols in colourless leaflets.

3'-Nitro-3-phenylphthalaz-1-one.—A solution of 5 g. of 1-hydroxy-(3'-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid in 25 c.c. f concentrated sulphuric acid was diluted with 30 c.c. of water, nd the mixture boiled (b. p. 140°) under reflux. Solution was omplete after ¾ hour, and boiling was continued for a further ¾ hour, etic acid being eliminated during the reaction. The mixture was ooled, diluted with 120 c.c. of water, boiled, and filtered. After ooling, the sulphate (colourless needles) was filtered off and neutraled with sodium carbonate. A further quantity was isolated by eutralising the filtrate. The united product was purified through ıe sparingly soluble hydrochloride (long, colourless needles), and, 'ter neutralisation with sodium carbonate, crystallised from yridine in pale yellow needles, m. p. 324° (yield 2·3 g.; 56·5%) 'ound: C, 63·2; H, 3·5; N, 15·7. $C_{14}H_9O_3N_3$ requires C, 62·9; , 3·4; H, 15·7%). The substance is readily soluble in glacial etic acid, soluble in nitrobenzene, sparingly soluble in alcohol and hyl acetate, and very sparingly soluble in benzene. It is insoluble sodium carbonate, and very sparingly soluble in boiling sodium ydroxide with a faint orange colour; with mineral acids it forms

salts, which are readily decomposed by water. With an alcoh solution of picric acid it forms a *picrate*, bright yellow needles, m 234°, which can be recrystallised from alcohol without decomp tion (Found: C, 48·6; H, 2·6; N, 16·8. $C_{20}H_{12}O_{10}N_6$ requi C, 48·4; H, 2·4; N, 16·9%).

Reduction of 3'-Nitro-3-phenylphthalaz-1-one.—(*a*) Reduction 3'-nitro-3-phenylphthalaz-1-one (5 g.) with aqueous sodium sulph as described for the 4'-nitro-isomeride (this vol., p. 2553) g 3'-amino-3-phenylphthalaz-1-one (yield 3·3 g.; 74%), identi with that obtained from 1-hydroxy-3-(3'-aminophenyl)tetrahyd phthalazine-4-acetic acid (p. 2560).

(*b*) Reduction with zinc dust and hydrochloric acid gave 3'-ami *N*-phenylphthalimidine (yield 83%), identical with that obtair from 3'-amino-3-phenylphthalaz-1-one (p. 2560).

Action of Methyl Sulphate on 3'-Nitro-3-phenylphthalaz-1-one.— solution of 3'-nitro-3-phenylphthalaz-1-one in nitrobenzene v treated with methyl sulphate as described for the 4'-nitro-isomer (*loc. cit.*), and the nitrobenzene removed by distillation with stea The aqueous residue, after being filtered from a little resin, gave orange-yellow, flocculent precipitate when rendered alkaline w sodium carbonate. This basic substance behaves with alcohol i similar manner to the 4'-nitro-isomeride, becoming first resinous a then crystalline. Thus, crystallisation from methyl alcohol g golden-yellow needles, m. p. 114—117° (Found: OMe, 18·5%), crystallisation from ethyl alcohol gave large, golden prisms, m 116—120° (Found: total OR, calculated as OMe, 18·1%). definite conclusions as to the composition of these compounds co be based on these analyses, however, because the substance combined with the alcohols, and the products are decompo partially even by drying in a vacuum at the air temperature, as done for the preparation of the analytical specimens; moreover 100° the crystals melt, then resolidify, and are converted gradu into 4-keto-1-methoxy-3-(3'-nitrophenyl)-3 : 4-dihydrophthalaz The latter change was best effected by heating first at 100° and t at 140°, and, unlike the case of the 4'-nitro-isomeride, in this inst there was always simultaneous formation of a certain amount more complex substance, red needles, m. p. 289°, especially if hea was too rapid at first.

4-*Keto*-1-*methoxy*-3-(3'-*nitrophenyl*)-3 : 4-*dihydrophthala* crystallised from alcohol in long, colourless, prismatic needles, n 182° (Found: C, 60·8; H, 3·9; N, 14·3; OMe, 10·2. $C_{15}H_{11}$C requires C, 60·6; H, 3·7; N, 14·1; OMe, 10·4%); it is rea soluble in chloroform, ethyl acetate, glacial acetic acid, and tolu

·ol insoluble in dilute mineral acids or alkalis. When 1 g. was ›ated with glacial acetic acid and twice the volume of hydrobromic ›id in a sealed tube at 100° for ½ hour, 1 : 4-*diketo*-3-(3′-*nitrophenyl*)-*trahydrophthalazine* separated on cooling, and after crystallisation ·om alcohol formed colourless needles, m. p. 280° (Found : C, 59·6; ., 3·3; N, 14·8. $C_{14}H_9O_4N_3$ requires C, 59·4; H, 3·2; N, 14·8%). · is insoluble in dilute mineral acids, but soluble in dilute sodium ırbonate with a pale yellow colour.

3′-*Nitro*-3-*phenylphthalaz*-4-*one*.—Alcoholic solutions of *o*-phthal-dehydic acid and *m*-nitrophenylhydrazine were boiled under reflux ; described for the 4′-nitro-isomeride (*loc. cit.*). After removal of ›out one-half of the alcohol, the *lactone* form of the phenylhydr-:one separated in small, orange crystals, m. p. 240° after becoming ›lourless at 200° (Found : C, 58·7; H, 4·0; N, 14·6. $C_{14}H_{11}O_4N_3$ ·quires C, 58·9; H, 3·9; N, 14·7%). It is sparingly soluble in lıte hydrochloric acid and soluble in dilute sodium carbonate, ıt acidification of the alkaline solution gave 3′-nitro-3-phenyl-ıthalaz-4-one and not the hydrazone, and the same substance ıs obtained in attempts to recrystallise the lactone form from cohol or pyridine. The *phthalazone* was prepared most con-:niently by boiling a nitrobenzene solution for a short time, and, ter cooling, crystallised in colourless needles, m. p. 240° (Found : 62·8; H, 3·5; N, 16·0. $C_{14}H_9O_3N_3$ requires C, 62·9; H, 3·4; , 15·7%). It is soluble in alcohol, insoluble in sodium carbonate hydroxide, and very sparingly soluble in hydrochloric acid. It ·ither forms a picrate nor reacts with methyl sulphate.

3′-*Amino*-3-*phenylphthalaz*-4-*one*.—To a fine suspension of 3′-nitro-phenylphthalaz-4-one in boiling water, made alkaline with sodium ·droxide, hydrosulphite was added until a clear solution was ·tained. After cooling, 3′-*amino*-3-*phenylphthalaz*-4-*one* separated, d on recrystallisation from water formed colourless needles, m. p. 6° (Found : C, 71·2; H, 4·8; N, 17·5. $C_{14}H_{11}ON_3$ requires C, ·9; H, 4·6; N, 17·7%). It forms a hydrochloride, clusters of lourless needles, and can be diazotised.

We desire to thank Alliance Colour and Chemical Co., and British ·estuffs Corporation for gifts of sodium β-naphthol-1-sulphonate.

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CCCXXXIX.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXXII. The Resolution of Phenylbenzylcarbinol.*

By WILLIAM GERRARD and JOSEPH KENYON.

IN view of the marked alterations in rotatory power and rotatory dispersion which are effected when an aromatic nucleus is introduced into the molecule of an aliphatic secondary alcohol (compare *inter alia*, Part XXV, J., 1925, **127**, 1094), it seemed desirable to study the effect of the introduction of two aromatic nuclei into the molecule of an aliphatic secondary alcohol.

With this object in view, the optically active modifications of phenylbenzylcarbinol have been prepared and their optical properties examined. The noteworthy results of this investigation are as follows: The effect of temperature on the rotatory power of the alcohol is very marked (Table I), there being a ten-fold increase on cooling from 125° to 20°, and the specific rotatory power of this alcohol at 20° is the largest yet recorded for a secondary alcohol; at the same time the rotatory dispersion ratio $\alpha_{4358}/\alpha_{5461}$ changes from 2·57 at 125° to 1·79 at 20°. The effect of solvents on the rotatory power is also very pronounced (Table II), the value of $[\alpha]_{5461}^{25°}$ changing from $-11·0°$ in pyridine solution to $+64·1°$ in ethyl-alcoholic solution, whilst in benzene solution the rotatory dispersion is anomalous. When the values of the specific rotatory powers of the alcohol in the homogeneous state are plotted against the squares of the wave-lengths of light used, the resulting curve is non-linear.

The acetate of *l*-phenylbenzylcarbinol, which is dextrorotatory, increases in rotatory power with rise of temperature, the values being given in Table III.

Phenylbenzylcarbinol has already been obtained in an optically active condition by Levene (*J. Biol. Chem.*, 1925, **65**, 507) by the method herein described, but the rotatory power obtained ($[\alpha]_D^{20°}$ $+ 18·54°$) indicates that the resolution was incomplete.

EXPERIMENTAL.

Phenylbenzylcarbinol was prepared by adding an ethereal solution of benzaldehyde (96 g.) to a vigorously stirred and ice-cold ethereal solution of benzyl magnesium chloride, prepared from 126 g. of benzyl chloride, and working up the product in the usual way. The crude carbinol (m. p. 61°) was purified by crystallisation from light petroleum containing 5% of benzene, being thus obtained as white needles, m. p. 67°, b. p. 177°/15 mm.; yield 154 g., 78%.

Phenylbenzylcarbinyl hydrogen phthalate, prepared by heating a mixture of the carbinol (120 g.) and phthalic anhydride (90 g., previously crystallised from dry chloroform to remove traces of phthalic acid) at 120° for 24 hours and working up the product in the usual manner, was obtained (192 g., 91%), after crystallisation from a mixture of ether and light petroleum, in small needles, m. p. 131° (Found, by titration with NaOH: *M*, 347. Calc.: *M*, 346).

d-*Phenylbenzylcarbinyl Hydrogen Phthalate.*—Quinine (110 g.) was dissolved in a hot solution of *dl*-phenylbenzylcarbinyl hydrogen phthalate (100 g.) in acetone (200 c.c.), and the resulting *d*A,*l*B salt, which separated on standing, was removed by filtration and recrystallised four times from 1½ times its weight of ethyl alcohol, the rotatory power of the *d*-phenylbenzylcarbinyl hydrogen phthalate obtained from it by decomposition having then become constant. The pure *quinine* salt forms soft, silky needles, m. p. 205° (decomp.), which are too insoluble in cold solvents to allow of its rotatory power being determined; it was dissolved in the minimum amount of hot alcohol and the solution poured into a slight excess of dilute hydrochloric acid; the precipitated *d*-hydrogen phthalic ester, after washing and drying, was crystallised from acetic acid (40 c.c. of 90%) and subsequently from ether–light petroleum, being obtained as fine needles, m. p. 131°; yield 31 g., a further 7 g. being obtained by working up the mother-liquors: $[\alpha]_D^{25^\circ}$ +32·75°, $[\alpha]_{5461}^{25^\circ}$ +38·75° (c = 5·0, in ethyl alcohol, 99%).

l-*Phenylbenzylcarbinyl Hydrogen Phthalate.*—The partially active *l*-hydrogen phthalic ester (50 g.; $[\alpha]_{5461}^{25^\circ}$ −30·7° in alcohol), obtained by the decomposition of the more soluble fractions of the quinine salt, was dissolved in methyl alcohol (150 c.c.) and the hot solution mixed with cinchonine (42·5 g.). The *l*A,*d*B salt, which separated from the solution on standing, after four recrystallisations from methyl alcohol containing 10% of acetone reached constancy of m. p., 110°, and of rotatory power, $[\alpha]_{5461}^{25^\circ}$ +82·3° (c = 4·90 in ethyl alcohol). The pure *cinchonine* salt was dissolved in hot alcohol and decomposition effected as described above. The recrystallised *l*-phenylbenzylcarbinyl hydrogen phthalate has m. p. 131° and $[\alpha]_{5461}^{25^\circ}$ −38·80° (c = 5·00 in ethyl alcohol); yield 31 g.

d- *and* l-*Phenylbenzylcarbinols.*—The free carbinols were obtained by gently boiling for 15 minutes the respective hydrogen phthalic esters with a slight excess of dilute aqueous sodium hydroxide. The liberated alcohols were extracted with ether and subsequently crystallised from ether–light petroleum; they each have m. p. 67°. Their rotatory powers are given in Table I.

l-*Phenylbenzylcarbinyl acetate* (l-αβ-*diphenylethyl acetate*), prepared

by the slow addition of acetyl chloride (3 g.) to a solution of *l*-phenylbenzylcarbinol (6 g.) in dry pyridine (15 c.c.), was obtained as a colourless oil (6·3 g.), b. p. 182°/15 mm. (Found, by hydrolysis with alcoholic potassium hydroxide: *M*, 241. $C_{16}H_{16}O_2$ requires *M*, 240); $[\alpha]_{5461}^{17^\circ}$ + 28·00°.

TABLE I.

Specific rotatory powers of *d*-phenylbenzylcarbinol in the homogeneous state at different temperatures.

	$[\alpha]_\lambda^{t^\circ}$.					
t.	4358.	5461.	5780.	5893.	6708.	$\frac{\alpha_{4358}}{\alpha_{5461}}$.
125°	+16·70°	+ 6·51°	+ 5·22°	+ 5·03°	+ 3·41°	2·569
115	20·59	8·68	7·21	6·70	4·98	2·373
100	28·65	12·92	11·18	10·30	7·42	2·217
90	35·00	16·57	14·38	13·39	10·32	2·112
80	41·61	20·40	17·68	16·80	12·85	2·039
70	51·00	25·40	22·12	20·64	16·06	2·007
60	61·90	31·82	27·88	26·11	20·20	1·945
By extrapolation:						
20	120·2	67·1	—	—	—	1·79

TABLE II.

(*a*) Specific rotatory powers of *d*-phenylbenzylcarbinol in various solvents (*c* = 5·00).

	$[\alpha]_\lambda^{25^\circ}$.					
Solvent.	4358.	5461.	5780.	5893.	6708.	$\frac{\alpha_{4358}}{\alpha_{5461}}$.
Pyridine	− 14·15°	−11·00°	−10·20°	− 9·81°	− 8·45°	1·28
Chloroform	− 12·02	− 9·71	− 9·10	− 8·50	− 7·65	1·24
Carbon disulphide	− 9·00	− 8·15	− 7·50	− 7·20	− 6·45	1·11
Benzene	− 0·20	− 3·00	− 3·00	− 3·00	− 3·00	0·07
Carbon tetrachloride	+ 6·90	+ 1·0	+ 0·6	+ 0·5	+ 0·2	6·9
Acetone	+ 44·63	+22·10	+19·1	+17·8	+13·7	2·19
Ethyl alcohol ... Ethyl alcohol (*l*-carbinol)	+120·8 —	+64·09 −64·04	+ 55·3	+52·8	+ 38·7	1·88
Ethyl alcohol (at *17°*)	*+126·8*	*+65·4*	*+57·2*	—	—	1·93

(*b*) Specific rotatory powers of *d*-phenylbenzylcarbinyl hydrogen phthalate in various solvents (*c* = 5·00).

Acetone	+32·8°	+14·71°	+12·50°	+12·01°	+11·00°	—
Benzene	− 9·71	− 9·1	− 9·0	− 8·9	− 7·7	—
Chloroform	− 5·3	− 5·1	− 4·7	− 4·6	− 4·3	—
Ethyl alcohol ...	+38·75	—	—	+32·75	—	—
Ethyl alcohol (*l*-ester)	−38·80	—	—	—	—	—

TABLE III.

Specific rotatory powers of the acetate of *l*-phenylbenzylcarbinol in the homogeneous state at different temperatures.

	$[\alpha]^{t°}_{\lambda}$.					
t.	4358.	5461.	5780.	5893.	6708.	$\frac{\alpha_{4358}}{\alpha_{5461}}$.
130°	+78·18°	+43·81°	+38·46°	+36·86°	+27·82°	1·784
120	76·54	43·09	37·92	36·18	26·66	1·776
110	74·94	42·02	37·26	35·38	26·31	1·776
90	70·98	40·33	35·62	34·49	25·25	1·760
80	66·43	38·06	33·22	31·81	23·85	1·745
50	59·75	35·15	30·28	29·00	22·02	1·698
30	52·24	31·09	27·07	25·65	19·61	1·680
17	47·12	28·00	24·52	23·51	17·69	1·682

The specific rotatory power of this ester determined at 17° was und to be unchanged after the above data had been obtained. portion of the ester was hydrolysed and the resulting carbinol ssessed a rotatory power identical with that of the carbinol from ich the ester was prepared. It is thus evident that no racemis- on had taken place during either the esterification or the subse- ent heating of the ester.

Determination of Densities.—

l-Phenylbenzylcarbinol: $d^{t°}_{4°}$ = 1·0358 at 70°, 1·0251 at 86°, ·210 at 92°, 1·0152 at 100°, 1·0095 at 110°, 1·0031 at 120°.

l-Phenylbenzylcarbinyl acetate: $d^{t°}_{4°}$ = 1·0831 at 17°, 1·0723 at °, 1·0552 at 50°, 1·0380 at 70°, 1·0214 at 90°, 1·0041 at 110°, ·958 at 120°, 0·9870 at 130°.

The authors desire to express their thanks to the Government ant Committee of the Royal Society for a grant which has helped defray the cost of this investigation.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, July 4th*, 1928.]

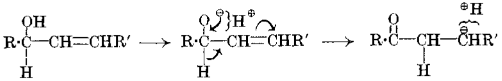
CCXL.—*The Mobility of Symmetrical Triad (Prototropic*) Systems. Part III. Three-carbon Prototropy in an αγ-Diphenylallyl Ether.*

By CHARLES WILLIAM SHOPPEE.

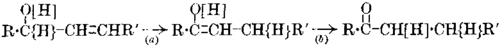
a recent communication (Burton and Ingold, this vol., p. 908, tnote), it was suggested that the transformation of α-arylated yl alcohols to saturated ketones in the presence of alcoholic alkali

* This word has been added to the serial title to indicate the exclusion of d *anionotropic* systems which are being concurrently investigated in these oratories.

(Tiffeneau, *Bull. Soc. chim.*, 1907, **1**, 1209; Nomura, *ibid.*, 1925, **37**, 1245) occurred through the pinacolic electron displacement:



Alternatively, the change may be regarded as proceeding by three-carbon prototropy (*a*) succeeded by ketonisation (*b*):



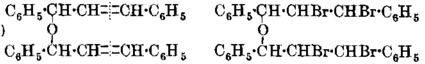
In a paper (Ingold, Shoppee, and Thorpe, J., 1926, 1480) dealing with the mechanism of tautomerism in the so-called three-carbon system CH·C:C·C:O (which, according to the view there advanced, is not a symmetrical triad system but a pentad keto-enol complex; see also Ingold, *Ann. Report*, 1927, **24**, 114), it was shown that hydroxyl, and still better ethoxyl, ions should be extremely powerful catalysts for the $\alpha\beta$-$\beta\gamma$ change. When the theoretical reason for this is examined, it is seen to apply not only to this special case, but to the whole of prototropy, and thus, having regard to the experimental conditions of the reaction considered by Burton and Ingold, it seemed possible that the mobility of a truly triad three-carbon system was under observation. Since this condition has not previously been established, except for systems involved in a ring (*e.g.*, indene; Ingold and Piggott, J., 1923, **123**, 1469; compare Goss and Ingold, this vol., p. 1268), the mechanism of the reaction referred to appeared worthy of study.

An attempt is now described to differentiate between the mechanisms formulated above by investigating an ether of type (I). Here pinacolic electron displacement cannot occur, for there can be no ionisation of the alkyl group R, with consequent formation of an electron source to constitute the driving force of the rearrangement. On the other hand, three-carbon prototropy can take place with

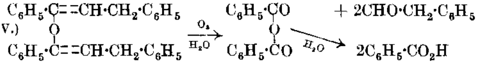
(I.) R′·CH(OR)·CH:CHR″ R′·C(OR):CH·CH_2R″ (II.)

production of the isomeride (II), corresponding with process (*a*) above, but the snbstituent R will prevent further change [process (*b*) above]. Thus, if pinacolic electron displacement is the mechanism underlying the first-mentioned transformation, an ether of type (I) will be unaffected by treatment with alcoholic sodium ethoxide; but if the rearrangement can take place by a three-carbon prototropic change, equilibration of the ethers (I) and (II) is to be anticipated.

The ether examined was *bis-αγ-diphenylallyl ether* (III), an ınsaturated crystalline solid which yields a *tetrabromide* (IV), and ›n fission with ozone gives benzaldehyde and benzoic acid.

(III.)  (IV.)

This ether was heated with alcoholic sodium ethoxide, and the ıbsence of an appreciable amount of phenyl β-phenylethyl ketone, vhich would be formed if hydrolysis of the ether linking occurred, vas shown by treatment with semicarbazide. The product was a iquid isomeric with the ether (III); it was shown to consist essentially f the ether (V), since on fission with ozone it yielded the products, henylacetaldehyde and benzoic acid, to be expected from a com- ›ound of this constitution.

V.) 

Treatment with bromine confirmed this structure, four atoms eing absorbed; the product, however, was not a saturated tetra- romide (VI) isomeric with (IV), but an unsaturated dibromide VII), evidently formed from (VI) as a consequence of the well- nown instability of halogens in α-halogeno-ethers (—O—C—Br):

$$\text{(VI.)}\ (CH_2Ph\cdot CHBr\cdot CBrPh)_2O \xrightarrow{-2HBr} (CH_2Ph\cdot CBr{:}CPh)_2O\ \text{(VII.)}$$

he position of equilibrium in hot alcoholic sodium ethoxide favours he isomeride (V) very largely, and it thus appears that the com- ined electronic affinities (inductive effect) represented in Ph>C(H)·C:C / RO are sufficient to produce (nnder the catalytic con- itions mentioned) tautomeric mobility in a three-carbon system hich is of a particularly simple type, since it is not implicated in a "developed" keto-enol complex.

Whether the reaction discussed by Burton and Ingold is to be epresented by the first or the second of the mechanisms formulated t the outset cannot yet be decided, but the possibility of the econd mechanism is clearly established by the example herein escribed.

EXPERIMENTAL.

Bis-αγ-diphenylallyl Ether (III).—αγ-Diphenylallyl alcohol was repared from cinnamaldehyde and phenyl magnesium bromide nd had m. p. 58° after crystallisation from ligroin (b. p. 40—60°).

The alcohol (15 g.), dissolved in glacial acetic acid, was treated with 75 g. of a 30% solution of hydrogen bromide in glacial acetic acid in the cold, and the mixture stirred for 2 hours. Pouring on ice, extraction with ether, washing (sodium hydrogen carbonate), drying, and evaporation of the ethereal extract yielded an oil which soon crystallised. After rubbing with a mixture of ether and ligroin, the *ether* was collected. It crystallised from ligroin (b. p. 60—80°), or from a large volume of methyl alcohol, in fine, rhombic prisms, m. p. 98—99° (Found : C, 89·5, 89·7; H, 6·6, 6·7. $C_{30}H_{26}O$ requires C, 89·5; H, 6·5%); yield, 13 g.

Bis-βγ-dibromo-αγ-diphenylpropyl Ether (IV).—The above ether (1·0 g.), dissolved in chloroform, was treated with a chloroform solution of bromine; absorption of 2 mols. took place readily, and removal of the solvent yielded a pale yellow oil (Found : C, 50·1; H, 3·9. $C_{30}H_{26}OBr_4$ requires C, 49·9; H, 3·6%).

Ozonolysis of the Ether (III).—A solution of the ether (2·0 g.) in glacial acetic acid was treated with ozonised oxygen, and after decomposition of the ozonides, the product was separated into neutral and acid fractions. The former had the characteristic odour of benzaldehyde, which was identified as the phenylhydrazone, m. p. 156°; the yield was small, but the acid fraction, which consisted entirely of benzoic acid, was correspondingly large.

Bis-αγ-diphenylpropenyl Ether (V).—The ether (III) (2·0 g.) was added to a solution of sodium (2·0 g.) in 99·5% ethyl alcohol (25 c.c.), and the mixture boiled under reflux for 2 hours on a sand-bath. The product was poured into much water and extracted with ether, and the dried extract evaporated. The yellow oil obtained (Found : C, 88·5; H, 6·5. $C_{30}H_{26}O$ requires C, 89·5; H, 6·5%) decomposed on distillation in a vacuum; it was treated with alcoholic semicarbazide acetate solution for a week, but no semicarbazone separated, and the oil was recovered by pouring the solution into water and extraction with ether.

Bis-β-bromo-αγ-diphenylpropenyl Ether (VII).—The crude ether (V) was treated with 2·5 mols. of bromine in chloroform solution. Addition took place at first, but hydrogen bromide was soon evolved. Hydrogen bromide and chloroform were removed by evaporation on the steam-bath; the oil obtained, which did not solidify when kept over potash in a vacuum, was dissolved in ether, and the solution filtered and evaporated. Analysis indicates that, although not quite pure, the product consists essentially of the dibromo-compound (VII) (Found : C, 62·0; H, 4·1. $C_{30}H_{24}OBr_2$ requires C, 64·3; H, 4·3%). It quickly decolorises an alkaline solution of permanganate in aqueous acetone.

Ozonolysis of the Ether (V).—The ether (2·0 g.), dissolved in glacial

cetic acid, was treated with ozonised oxygen. After decomposition of the ozonides, the product was separated into neutral and acid ractions. The former on treatment with alcoholic semicarbazide cetate solution yielded a fluffy precipitate after several days absence of benzaldehyde); this was filtered off, and after two rystallisations from methyl alcohol, separated in needles, m. p. 53°, identified as phenylacetaldehydesemicarbazone. The acid raction was systematically crystallised from ligroin; benzoic acid as obtained, but no trace of phenylacetic acid could be detected.

Phenyl β-Phenylethyl Ketone Semicarbazone.—The ketone, m. p. 2—73°, prepared by the method of Perkin and Stenhouse (J., 1891, 9, 1007), was treated with alcoholic semicarbazide acetate solution, nd the *semicarbazone* crystallised out during 24 hours; it separated rom dilute alcohol in needles, m. p. 144° (Found: C, 72·0; H, 6·4. $C_{16}H_{17}ON_3$ requires C, 71·9; H, 6·4%).

The author wishes to express his thanks to Professor C. K. Ingold, F.R.S., for his interest and advice, and to the Royal Commissioners f the 1851 Exhibition for a Senior Studentship.

THE UNIVERSITY, LEEDS. [*Received, August 16th*, 1928.]

CCXLI.—*Conditions of Formation of Rings attached to the* o-, m-, *and* p-*Positions of the Benzene Nucleus. Part III.*

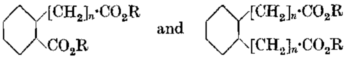
By ALAN FRANCIS TITLEY.

IN Part I of this series (J., 1922, **121**, 1562) the scope of the proposed nvestigation was defined as (i) the determination of the limit of ize of rings which can be attached to the ortho-positions of the enzene nucleus, and (ii) an enquiry into the possibility of synhesising such rings in the meta- and para-series.

The synthesis of rings of this second type had been previously laimed by von Braun and his collaborators (*Ber.*, 1912, **45**, 1274; 918, **51**, 1217, 1225; 1919, **52**, 2015; 1925, **58**, 281), and in one ase (von Braun, Karpf, and Garn, *Ber.*, 1920, **53**, 98) a supposed eterocyclic "meta-ring" was converted into a homocyclic ring. t was shown, however, in Part II of this series (J., 1926, 508), that n this particular instance both the supposed heterocyclic and omocyclic "meta-rings" of von Braun were in reality benzene ompounds containing simple side-chains in the meta-positions.

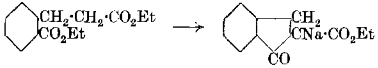
In the present communication some further results of the

application of the Dieckmann reaction (the standard reacti chosen) to esters of the type

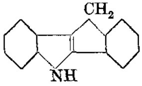


are described, together with some attempts to effect meta- a para-ring closure by the same methods.

Five-membered Ring.—The formation of a five-membered ring b the action of sodium on *o*-phenylenediacetic ester was described i Part I (*loc. cit.*). It is now found that condensation occurs, thoug less readily, when one of the reacting carbethoxy-groups is directl attached to the benzene nucleus. Thus, sodium reacts with toluene solution of *ethyl* β-o-*carbethoxyphenylpropionate* (I) at 100 forming ethyl sodio-1-hydrindone-2-carboxylate (II), about 20% the ester (I) apparently being saponified. Acidification of th

(I.)  (II.)

sodium derivative yielded ethyl 1-hydrindone-2-carboxylate (com pare Mitchell and Thorpe, J., 1910, **97**, 2273), which was hydrolyse almost quantitatively by acids or alkalis to 1-hydrindone (compa Part I, p. 1563). The phenylhydrazone of this ester, or a mixtu of it with dry phenylhydrazine hydrochloride, was converted b concentrated hydrochloric acid into 2 : 3-*indeno*(1 : 2)-*indole* (III

(III.) 

$C_6H_4{<}^{CH_2}_{CO}{>}C{<}^{CH_3}_{CO_2Et}$ (IV.)

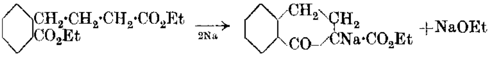
the *N*-methyl compound of which has been described by Armit an Robinson (J., 1922, **121**, 838).

Ethyl 2-methyl-1-hydrindone-2-carboxylate (IV) was readil obtained by the action of methyl iodide on (II) (Mitchell an Thorpe, *loc. cit.*). The introduction of the methyl group into th 1-hydrindone ring appears to decrease the reactivity of the ketoni grouping, since, unlike the 1-methyl-2-hydrindone-1-carboxyli ester, the above ester does not readily form a phenylhydrazone or semicarbazide. In both esters, however, the stability of the ring i decreased. Thus, on hydrolysis, (IV) yields, in addition to 2-methyl 1-hydrindone (Mitchell and Thorpe, *loc. cit.*), β-o-*carboxyphenyliso butyric acid*. These results are of some importance in connexio

with those obtained in attempting to prepare meta- and para-ring structures.

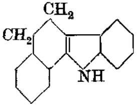
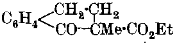
Six-membered Ring.—The formation of ketotetrahydronaphthalenecarboxylic acids by the dehydration of various γ-phenylbutyric acids has been investigated by Attwood, Stevenson, and Thorpe (J., 1923, **123**, 1755), who have shown that β-substituted phenylbutyric acids, which contain in addition another carboxyl group, readily yield the six-membered ring under the action of sulphuric acid at room temperature. Unsubstituted phenylbutyric acid, however, according to Krollpfeiffer and Schäfer (*Ber.*, 1923, **56**, 620), is not dehydrated at room temperature and only to the extent of 50% at 100°.

The " internal acetoacetic ester " condensation



gives a 70% yield in toluene at 100°, and therefore does not take place so readily as either of the two reactions previously described leading to the formation of five-membered rings.

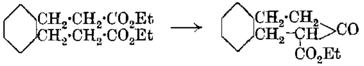
Ethyl 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate (compare Hückel and Goth, *Ber.*, 1924, **57**, 1285) is almost quantitatively converted on hydrolysis with acids or alkalis into 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (α-tetralon); it does not give a crystalline phenylhydrazone but, on treatment with phenylhydrazine hydrochloride and hydrochloric acid, it yielded 1 : 2-*indolo*(2 : 3)-3 : 4-*dihydronaphthalene* (V), and its sodio-derivative is methylated by methyl iodide to *ethyl* 1-*keto*-2-*methyl*-

(V.)   (VI.)

1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylate* (VI); by acid hydrolysis (VI) is quantitatively converted into 1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, whilst alkaline hydrolysis yields a mixture of this ketone with γ-o-*carboxyphenyl*-α-*methylbutyric acid*, again pointing to a destabilisation of the saturated ring on the addition of a methyl group.

Seven-membered Ring.—*o*-Phenylenedipropionic ester (VII) was found to be only slowly attacked by finely divided sodium in toluene at 100°, being almost entirely saponified; about 2—3%, however,

condensed to give (VIII), which was characterised by means of its *phenylhydrazone*. From these results the formation of a seven-

(VII.)  (VIII.)

membered ring by the condensation of two three-membered side-chains in the ortho-position does not appear to be easily brought about. The formation of 1-ketophenheptamethylene from δ-phenyl-valeryl chloride by the Friedel–Crafts reaction (Kipping and Hunter, J., 1903, **83**, 246) and the more recent work of von Braun and Bayer (*Ber.*, 1927, **60**, 1257) suggest, however, the probability that ring-closure by means of the Dieckmann reaction on *o*-carboxy-phenylvaleric ester might be more readily effected.

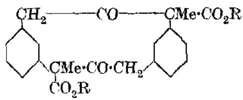
m- *and* p-*Ring-closure*.—From the theoretical standpoint there appears to be no valid reason why meta- and para-ring structures should not be capable of a stable existence, but the uncertainty of the benzene structure and the possibility that the rings would not be co-planar render it difficult to predict the most favourable conditions for their formation. The attempts described below to prepare such rings by the methods used for ortho-ring formation led to no conclusive result, but illustrate the difficulties of the problem. The action of sodium at 100° on toluene solutions of the following esters was investigated (R = Me or Et):

	meta-Series.	*para*-Series.
$C_6H_4<^{X-CO_2R}_{Y-CO_2R}$	(IX): $X=C_2H_4$; $Y=C_2H_4$.	(X): $X=C_2H_4$; $Y=C_2H_4$.
	(XI): X = — ; $Y=C_2H_4$.	(XII): X = — ; $Y=C_2H_4$.
	(XIII): $X=CH_2$; $Y=CH_2$.	(XIV): $X=CH_2$; $Y=CH_2$.
	(XV): $X=CH_2$; Y = — .	

Certain regularities of behaviour were observed. Thus (IX) and (X) (R = Et) and (XII) (R = Me) were only very slowly acted on by sodium with gradual formation of the sodium salt of the acid. There was no trace of ring-formation or condensation reactions. On the other hand, (XI) (R = Me), (XIII) and (XIV) (R = Me and Et), and (XV) (R = Me) reacted with sodium almost as readily as the corresponding ortho-esters under the same conditions, giving mixtures of sodium salts of the acids with unstable condensation products of varying degrees of molecular complexity, which could not be purified by distillation.

By employing the methyl esters, however, and methylating the resulting sodium compounds with methyl iodide, the products of the reaction could be separated by distillation under greatly reduced pressure. In addition to highly complex condensation products,

bimolecular compounds were isolated, presumably of "bridged-ring" structure of the type shown (from XIII).



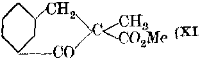
Finally, in each case a lower-boiling product was obtained, consisting mainly of the dimethyl ester, regenerated by the action of the methyl iodide on the disodium salt of the acid which had been produced in the original reaction. The hydrolysis of these low-boiling fractions yielded, in the case of (XIII) and (XIV), not only the simple acids, but also small quantities of the α-methylated acids (XVI) and (XVII), respectively. From (XI), the α-methylated acid

(XVI.) $m\text{-}C_6H_4<^{CHMe\cdot CO_2H}_{CH_2\cdot CO_2H}$ $\quad\quad$ $p\text{-}C_6H_4<^{CHMe\cdot CO_2H}_{CH_2\cdot CO_2H}$ (XVII.)

(XVIII) was similarly obtained, the position of the methyl group in this instance being settled by synthesising the acid for comparison. On the other hand, no α-methylated acid was obtained in this way from (XV).

These two facts appeared to render it doubtful whether the formation of these α-methylated acids could be safely attributed to direct methylation of an α-methylene group, in each open-chain ester, which had been rendered slightly "acid" in character by its position between the phenyl and carbethoxy-groupings. It appeared possible that traces of meta- and para-ring compounds, *e.g.*, of the type (XIX) from (XI), were actually present in the low-boiling fractions, which gave rise to the α-methylated acids, *e.g.*, (XVIII), on hydrolysis. The low-boiling fractions were carefully

(XVIII.) $m\text{-}C_6H_4<^{CH_2\cdot CHMe\cdot CO_2H}_{CO_2H}$



(XIX.)

examined for traces of ketonic substances, but none could be detected. The possibility is nevertheless not entirely excluded because, as previously mentioned, the keto-group in methylated hydrindonecarboxylic esters of the normal type is not very reactive.

The mechanism by which the esters appear to be directly converted in toluene solution into the sodium salts of the corresponding acids is somewhat obscure and is being further investigated.

E X P E R I M E N T A L.

β-o-*Carboxyphenylpropionic Acid*.—*o*-Aldehydobenzoic acid (25 g.) is condensed with malonic acid (45 g.) in glacial acetic acid (20 g.) in presence of anhydrous sodium acetate (15 g.). The

mixture is heated for 8—10 hours at 100°, cooled, and diluted with 150 c.c. of water, whereby monohydrated phthalideacetic acid, m. p. 102—104°, is precipitated in nearly quantitative yield. (Drying in a steam-oven gives the anhydrous acid, m. p. 151°; compare Edwards, J., 1926, 813.) This condensation may also be effected in dry pyridine solution containing a trace of piperidine, the yield being practically the same. The acid is boiled with an excess of 25% sodium hydroxide for about 2 hours, cooled in ice, and acidified with the theoretical quantity of dilute hydrochloric acid; *o*-carboxycinnamic acid then separates as a thick pasty mass, which is filtered and washed with a large volume first of cold and then of boiling water. The crude acid melts at 194°, and after recrystallisation from alcohol forms small prisms, m. p. 197° (Found: C, 62·5; H, 4·2. Calc. for $C_{10}H_8O_4$: C, 62·5; H, 4·2%). Ehrlich (*Monatsh.*, 1888, **9**, 528), Edwards (*loc. cit.*), and Gabriel give m. p. 184°, 182°, and 173—175° respectively, but the acid passes into phthalideacetic acid on melting, for on re-melting it has m. p. 151°.

The *o*-carboxycinnamic acid is reduced by means of sodium amalgam to *o*-carboxyphenylpropionic acid, m. p. after recrystallisation 167° (Bamberger, *Ber.*, 1890, **23**, 1562, gives m. p. 165°); esterification of the latter acid by saturation of its boiling solution in ethyl alcohol with dry hydrogen chloride gives the *ethyl* ester, b. p. 182—183°/14 mm. (Found: C, 67·0; H, 7·11. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·20%).

Ethyl 1-*Hydrindone*-2-*carboxylate*.—Metallic sodium (5 g.) is finely granulated by shaking under boiling toluene (100 g.), and a solution of *o*-carboxyphenylpropionic ester (24 g.) in toluene (50 g.) is added. The reaction proceeds smoothly at 100° and is complete in 4—5 hours; the resulting sodium compound (II) dissolves to a considerable extent in the toluene (compare Sidgwick and Brewer, J., 1925, **127**, 2381) and is precipitated on addition of dry ether. On decomposition with dilute acid, 1-hydrindone-2-carboxylic ester separates as an orange oil, b. p. 179—180°/15 mm. (slight decomp.) (Found: C, 70·8; H, 6·0. Calc.: C, 70·6; H, 5·9%) (Mitchell and Thorpe, *loc. cit.*, give b. p. 185°/20 mm.); the phenylhydrazone (Found: C, 73·5; H, 6·35; N, 9·5. Calc.: C, 73·5; H, 6·1; N, 9·5%) has m. p. 103° (Mitchell and Thorpe, *loc. cit.*, give m. p. 101·5°).

Hydrolysis. The ester (5 g.) was mixed with an aqueous solution of 2·5 g. of sodium hydroxide and kept at room temperature for 24 hours; α-hydrindone separated as an oil in almost quantitative yield; b. p. 164—166°/20 mm., m. p. 39°. The phenylhydrazone had m. p. 130° (compare Liebermann, *Ber.*, 1898, **31**, 2081).

2 : 3-*Indeno*(1 : 2)-*indole* (III).—1-Hydrindone-2-carboxylic ester (4 g.), mixed with dry phenylhydrazine hydrochloride (2·8 g.) and

two drops of concentrated hydrochloric acid, is heated first on the water-bath and afterwards at 150° for about 2 minutes; the solid brownish cake is broken up, washed with water, and extracted with hot methyl alcohol. On cooling, small brownish-red plates are deposited, m. p. 251° (Found: N, 6·6. $C_{15}H_{11}N$ requires N, 6·8%).

Ethyl 2-Methyl-1-hydrindone-2-carboxylate.—1-Hydrindone-2-carboxylic ester (10 g.) was converted into the sodium derivative by adding its ethereal solution to sodium previously granulated under toluene. The bright yellow, flocculent mass was collected, washed with a little dry ether, suspended in 100 c.c. of alcohol and boiled with 10 g. of methyl iodide for 3 hours. The ester which separated on addition of water boiled at 166°/14 mm. (Mitchell and Thorpe, *loc. cit.*, give b. p. 181°/20 mm.) and solidified in long prisms, m. p. 31° (Found: C, 71·5; H, 6·5. Calc. for $C_{13}H_{14}O_3$: C, 71·5; H, 6·4%). The ester, on boiling with 20% methyl-alcoholic potash, was hydrolysed to the extent of about 60% to 2-methyl-1-hydrindone, b. p. 125—126°/18 mm. (Found: C, 81·8; H, 6·8. Calc.: C, 82·2; H, 6·8%), and to the extent of about 40% to β-o-*carboxyphenyliso-butyric acid*, colourless needles, m. p. 141° (Found: C, 63·4; H, 5·8. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8%).

Ethyl γ-o-*Carbethoxyphenyl*-n-*butyrate*.—The acid was obtained by the method of Hückel and Goth (*loc. cit.*), and its *ethyl* ester, prepared in the usual manner, had b. p. 188—189°/14 mm. (Found: C, 68·0; H, 7·7. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%).

Ethyl 1-Keto-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate.—The preceding ester (19 g.) was slowly added to sodium (3·5 g.) dispersed in toluene (100 g.). The reaction was complete after 6—7 hours at 100°. After addition of a little alcohol to decompose traces of unchanged sodium, powdered ice was added, and the mixture made just acid by the addition of 15 c.c. of concentrated hydrochloric acid. The toluene layer was separated, washed with sodium carbonate solution, dried, and the solvent removed under diminished pressure; 10 g. of crude 1-ketotetrahydronaphthalene-2-carboxylic ester (65% yield) were obtained, b. p. 183°/15 mm., m. p. 33° (Hückel and Goth give m. p. 34°). From the aqueous layer and sodium carbonate washings 3—4 g. of o-carboxyphenylbutyric acid were obtained on evaporation.

When warmed to 150° with the calculated quantity of phenylhydrazine hydrochloride and a little concentrated hydrochloric acid, the foregoing ester yields 1 : 2-*indolo*(2 : 3)-3 : 4-*dihydronaphthalene* (V), dark reddish plates, m. p. 161° (Found: N, 6·3. $C_{16}H_{13}N$ requires N, 6·4%).

Ethyl 1-Keto-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate (VI).—An alcoholic solution of 11 g. of the ketonic ester is

added to 1·2 g. of sodium, previously dissolved in 20 c.c. of eth alcohol. After the addition of 15 g. of methyl iodide, the mixtu is boiled for 2—3 hours, evaporated to a small bulk, and poured in water. The *methyl* compound separates as a colourless oil with terpene-like odour; b. p. 183—184°/18 mm. (Found: C, 72·(H, 6·9. $C_{14}H_{18}O_3$ requires C, 72·4; H, 6·9%). On steam dist lation with 20% sulphuric acid, this is converted into 1-*keto*-2-*meth tetrahydronaphthalene*, b. p. 143°/20 mm. (Found: C, 82·0; H, 7· $C_{11}H_{12}O$ requires C, 82·5; H, 7·5%), whereas alkaline hydrolysis wi 10% methyl-alcoholic potash gives a mixture of the above keto with γ-o-*carboxyphenyl*-α-*methylbutyric acid*, prisms, m. p. 17 (Found: C, 64·9; H, 6·6. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3% The decrease in stability of the saturated ring on the addition the methyl group is very strikingly exemplified in this instanc since the unmethylated ester is hydrolysed to *o*-carboxypheny butyric acid only by sodium and boiling *cyclo*hexanol, and then t an extent of not more than 20%.

Ethyl o-*Phenylenedipropionate* (VII).—The acid was prepared b the method of Perkin (J., 1888, **53**, 18); after purification by mea of the diethyl ester, it had m. p. 168° (Perkin found m. p. 160—162 "not very sharply"). The *ethyl* ester had b. p. 200—202°/12 mn (Found: C, 69·0; H, 7·8. $C_{16}H_{22}O_4$ requires C, 69·1; H, 7·9%).

Action of sodium on the ethyl ester. To sodium (1·8 g.), disperse in toluene (60 g.), was added *o*-phenylenedipropionic ester (11·5 g dissolved in toluene (15 g.), and the mixture heated on the wate bath. After 9 hours, the toluene was filled with a deposit of brow sodium compounds and no unchanged metallic sodium could b detected. The sodium derivatives were filtered off rapidly washed with dry ether, and decomposed with dilute hydrochlori acid. The brown, flocculent, oily material which separated wa extracted with ether, and the ethereal solution thoroughly washed with sodium carbonate solution; on acidification of these sodium carbonate washings, a large quantity of a brownish powder was precipitated, which, after recrystallisation from dilute alcohol, formed microscopic prisms, m. p. 167—168°, and was found on analysis to be *o*-phenylenedipropionic acid; this acid (9 g.) constituted the main product of the reaction. From the ethereal solution was obtained about 0·5 g. of a brownish oil of b. p. approx. 190°/15 mm., which gave an immediate purple colour with ferric chloride. The amount was not sufficient for purification but, on warming with phenylhydrazine at 100° and then adding alcohol, a crystalline *phenylhydrazone* was obtained which formed straw-yellow needles, m. p. 198° (decomp.), from hot alcohol (Found: C, 74·6; H, 6·8; N, 8·55. $C_{20}H_{22}O_2N_2$ requires C, 74·5; H, 6·8; N, 8·7%).

This phenylhydrazone is thus almost certainly derived from *ethyl 3-ketophenheptamethylene-2-carboxylate* (VIII).

Action of Sodium on m- *and* p-*Phenylenediacetic Esters.*

These esters are conveniently obtained from the corresponding nitriles (see Part II, *loc. cit.*) by simultaneous hydrolysis and esterification by means of the appropriate alcohol saturated with dry hydrogen chloride. *Methyl* m-*phenylenediacetate* has b. p. 185—187°/15 mm. (Found: C, 64·9; H, 6·3. $C_{12}H_{14}O_4$ requires C, 64·8; H, 6·3%). *Ethyl* m-*phenylenediacetate* has b. p. 188—189°/12 mm. (Found: C, 66·8; H, 7·3. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·2%). *Methyl* p-*phenylenediacetate* has b. p. 189—190°/15 mm. (Found: C, 64·6; H, 6·2%). *Ethyl* p-*phenylenediacetate* has m. p. 59° (Found: C, 66·9; H, 7·1%).

Ethyl *m*-phenylenediacetate (48 g.) was slowly added to metallic sodium (10 g.) finely granulated under toluene (150 g.). On warming on the water-bath, a vigorous reaction set in which was complete in about 20 minutes. The mass of brown sodium compounds was filtered off quickly, washed with a large volume of dry ether, and dried in a vacuum. An iodoform test showed that considerable quantities of sodium ethoxide were present. The sodium compounds were decomposed with the theoretical quantity of ice-cold dilute hydrochloric acid and the viscous yellow product was extracted with ether. Free *m*-phenylenediacetic acid was removed by shaking with dilute sodium carbonate, and the ethereal solution dried and distilled. The syrup so obtained, on removal of the last traces of ether in a vacuum, set to a solid sticky mass, which softened and melted at 30—40° and decomposed vigorously above 100° (Found: C, 70·8; H, 6·3. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%). This compound showed no tendency to crystallise on standing for 9 months or on cooling to −40°, whilst attempts at distillation under pressures as low as 0·3 mm. led to complete decomposition, with formation of a horny, shellac-like mass. The alcoholic solution gave a deep purple colour with ferric chloride and a deep green copper salt with copper acetate, indicating the presence of a keto-enol structure, but no crystalline compound with phenylhydrazine could be isolated. Hydrolysis with alcoholic potash gave rise to yellowish, insoluble resins.

Almost precisely similar results were obtained with ethyl *p*-phenylenediacetate, but the syrupy product obtained combined fairly readily with phenylhydrazine, yielding an amorphous, red, glassy mass. This was extracted with boiling methyl alcohol, and the solution poured into a large volume of dry ether. A small quantity of microscopic yellow needles was obtained which softened at 190°

and melted at 194—195° (Found: C, 73·6; H, 6·3; N, 9·5. $C_{18}H_{18}O_2N_2$ requires C, 73·5; H, 6·1; N, 9·5%). As this *phenylhydrazone* was obtained in very small yield and its molecular weight was not determined, it cannot be regarded as positive evidence of the formation of a *p*-β-hydrindonecarboxylic ester.

The action of sodium on the two dimethyl esters was carried out in a similar manner. The sodium compounds were mixed with dry methyl alcohol and a slight excess of methyl iodide and boiled for 12 hours. The solution was then poured into water, and the methylated product extracted with ether, dried, and distilled under 1 mm. pressure. Starting with methyl *m*-phenylenediacetate, three main fractions were obtained: (*a*) b. p. 131—135°, (*b*) b. p. 217—222°, (*c*) 270° and upwards; (*c*) was not further investigated, as it appeared to be of a high degree of molecular complexity. The *compound* constituting the middle fraction (*b*) probably has the bridged-ring structure (p. 2575) (Found: C, 70·2; H, 6·3; *M*, cryoscopic in acetic acid, 418. $C_{24}H_{24}O_6$ requires C, 70·6; H, 5·9%; *M*, 408); on hydrolysis with 2—3% methyl-alcoholic potash it gives about a 40% yield of a colourless, amorphous powder, which is insoluble in sodium carbonate but dissolves in warm dilute sodium hydroxide. This *substance,* which appears to be a lactone or acid anhydride, sinters at 340° and melts fairly sharply at 345—346° (Found: C, 72·5; H, 5·1. $C_{22}H_{18}O_5$ requires C, 72·9; H, 5·0%).

The low-boiling fraction (*a*) redistilled at 182—190°/15 mm. and could not be further separated by fractionation. After hydrolysis with dilute methyl-alcoholic potash, the crude acid obtained was extracted with cold chloroform until the insoluble residue melted sharply at 169° (pure *m*-phenylenediacetic acid). The soluble portion was fractionally recrystallised from water to remove traces of the above acid from the more soluble *phenylene*-1-*acetic*-3-α-*propionic acid* (XVI), m. p. 132° (Found: C, 63·6; H, 6·0. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8%).

The action of sodium on methyl *p*-phenylenediacetate gave similar results. The middle fraction had b. p. 225—228°/1 mm. (Found: C, 70·3; H, 6·2. $C_{24}H_{24}O_6$ requires C, 70·6; H, 5·9%). On hydrolysis, the low-boiling fraction (188—192°/16 mm.) gave a mixture of *p*-phenylenediacetic acid, m. p. 244°, and *phenylene*-1-*acetic*-4-α-*propionic acid* (XVII), m. p. 189° (Found: C, 63·3; H, 5·9. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8%).

Action of Sodium on m- *and* p-*Carboxyphenylpropionic Esters.*

Preparation of Esters.—*m*-Carboxyphenylpropionic acid was prepared by condensing *iso*phthalaldehydic acid (Davies, Perkin,

and Clayton, J., 1922, **121**, 2215) with malonic acid in glacial acetic acid or pyridine to obtain *m*-carboxycinnamic acid, needles, m. p. 275° (corr.) (Simonis, *Ber.*, 1912, **45**, 1584, gives m. p. 264°) (Found: C, 62·5; H, 4·3. Calc.: C, 62·5; H, 4·2%), and reducing this with sodium amalgam and sodium carbonate solution to m-*carboxyphenylpropionic acid*, plates, m. p. 177° (Found: C, 61·6; H, 5·25. $C_{10}H_{10}O_4$ requires C, 61·8; H, 5·2%). The *methyl* ester, prepared from this in the usual way, had b. p. 184—185°/15 mm. (Found: C, 64·9; H, 6·5. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%).

p-Carboxyphenylpropionic acid was prepared by two methods. (1) *p*-Toluoyl chloride (1 mol.) treated at 185—190° with bromine (2 atoms) gave a mixture of ω-bromo-*p*-toluoyl chloride, b. p. 155—156°/20 mm., and ω-*bromo*-p-*toluoyl bromide*, b. p. 170—171°/20 mm., m. p. 56° (Found: Br, 57·8. $C_8H_6OBr_2$ requires Br, 57·5%), together with some high-boiling material which was not distilled but appeared to consist of a mixture of ωω-dibromo-*p*-toluoyl chloride and bromide, since, on mixing with alcohol it yielded *ethyl* ωω-*dibromo*-p-*toluate*, hexagonal prisms, m. p. 103° (Found: C, 36·8; H, 3·08. $C_{10}H_{10}O_2Br_2$ requires C, 37·2; H, 3·10%). *Ethyl* ω-*bromo*-p-*toluate*, prepared from the mixture of monobromo-acid chloride and bromide, has b. p. 165°/18 mm. and crystallises in needles, m. p. 35—36° (Found: Br, 32·7. $C_{10}H_{11}O_2Br$ requires Br, 32·9%); when condensed with chloromalonic ester, it gives a fair yield of *ethyl chloro*-p-*carbethoxybenzylmalonate*, b. p. 235°/20 mm., m. p. 54—55° (Found: Cl, 9·95. $C_{17}H_{21}O_6Cl$ requires Cl, 9·81%), which, on reduction with zinc dust and acetic acid, yields *ethyl* p-*carbethoxybenzylmalonate*, b. p. 218—219°/15 mm. (Found: C, 62·8; H, 6·6. $C_{17}H_{22}O_6$ requires C, 63·2; H, 6·8%). On hydrolysis this is converted into p-*carboxybenzylmalonic acid*, a microcrystalline powder, m. p. 186—188° (Found: C, 55·5; H, 4·6. $C_{11}H_{10}O_6$ requires C, 55·4; H, 4·3%). The dicarboxylic acid does not lose carbon dioxide readily, but on heating to 240° it is converted into *p*-carboxyphenylpropionic acid, m. p. 294° (Found: C, 62·0; H, 5·2. Calc.: C, 61·8; H, 5·2%). The yields in the last stages of this synthesis are not good.

(2) The condensation of terephthalaldehydic acid with malonic acid gave a good yield of *p*-carboxycinnamic acid, a highly insoluble powder which, after subliming a little from 350° upwards, melts at 358° (decomp.) (Löw, *Annalen*, 1885, **231**, 367, gave no m. p.) (Found: C, 62·7; H, 4·3. Calc.: C, 62·5; H, 4·2%). The acid cannot be purified by recrystallisation, and this is best effected by converting it into the *ethyl* ester, which crystallises from dilute alcohol in prisms, m. p. 52° (Found: C, 67·5; H, 6·5. $C_{14}H_{16}O_4$ requires C, 67·8; H, 6·5%). On reduction of *p*-carboxycinnamic

acid with sodium amalgam and sodium carbonate, *p*-carboxyphenyl propionic acid, m. p. 294° (compare above) is obtained (Moses, *Ber.* 1900, **33**, 2626, gave m. p. 280°). The *methyl* ester crystallise from chloroform in prisms, m. p. 33° (Found: C, 64·6; H, 6·47 $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%).

Methyl *m*-carboxyphenylpropionate (27 g.), dissolved in toluene (20 g.), was added to sodium (5·6 g.) dispersed in toluene (60 g.), and the mixture heated for 12 hours on the water-bath. The sodium compounds were filtered off rapidly, washed with ether, suspended in 100 g. of dry methyl alcohol and, after the addition of 40 g. of methyl iodide, boiled for 3 hours. On distilling the product under 1 mm. pressure, two fractions were obtained at about 140°/1 mm. and 275°/1 mm. The low-boiling fraction redistilled at 183—187°/15 mm. and weighed 7·2 g. (Found: C, 66·0; H, 6·5%); 7 g. were hydrolysed in a sealed tube at 100° with 15 g. of 10% methyl-alcoholic potash, and on addition of water a clear brown solution was obtained, there being no evidence of ketone formation. The acidified solution was extracted with ether and yielded 6 g. of acid; two treatments of this crude product with 30 g. of cold chloroform extracted 1·55 g. and the residue then had m. p. 177°, thus being pure *m*-carboxyphenylpropionic acid. The chloroform-soluble acid was recrystallised several times from chloroform and finally from water to constant m. p. 137—138° (corr.) (Found: C, 63·6; H, 5·8. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8%). It was proved to be β-m-*carboxyphenyl*iso*butyric acid* (XVIII) by the following synthesis.

m-Toluoyl chloride was chlorinated at 160—165°, until the gain in weight was equivalent to one atom of chlorine. This gave a 90% yield of ω-*chloro*-m-*toluoyl chloride*, b. p. 149—150°/20 mm. (Found: Cl, 37·2. $C_8H_6OCl_2$ requires Cl, 37·6%), which on mixing with alcohol yielded *ethyl* ω-*chloro*-m-*toluate*, b. p. 168—169°/25 mm. (Found: C, 60·2; H. 5·7; Cl, 17·6. $C_{10}H_{11}O_2Cl$ requires C, 60·4; H, 5·5; Cl, 17·9%). This chloro-ester condensed with sodiomethylmalonic ester to give *ethyl* m-*carbethoxybenzylmethylmalonate*, which distilled without decomposition at 234°/24 mm. (Found: C, 63·8; H, 7·0. $C_{18}H_{24}O_6$ requires C, 64·3; H, 7·1%). The corresponding *acid*, obtained on hydrolysis, is a microcrystalline powder fairly soluble in water, m. p. 182—183° (decomp.). On heating to 185° until no more carbon dioxide is evolved, it is converted into β-*m*-carboxyphenyl*iso*butyric acid. The crude product had m. p. 136—137°, but after conversion to the *methyl* ester, b. p. 182°/18 mm., distilling, and re-hydrolysing, it crystallised from water in small prisms, m. p. 138—139° (Found: C, 63·7; H, 5·9%). The mixed m. p. of this acid with that obtained above was 138°.

m- *and* p-*Phenylenedipropionic Esters*.—The respective acids were obtained by the method of Kipping (J., 1888, **53**, 21). *Ethyl* m-*phenylenedipropionate* has b. p. 197—198°/15 mm. (Found: C, 68·8; H, 7·95. $C_{16}H_{22}O_4$ requires C, 69·1; H, 7·9%). *Ethyl* p-*phenylenedipropionate* crystallises in plates, m. p. 69° (Found: C, 68·9; H, 7·8%).

My thanks are due to the Ramsay Memorial Trustees for a Fellowship, during the tenure of which the greater part of this work was carried out, and to Professor W. H. Perkin for his advice.

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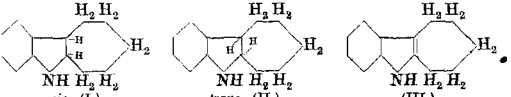
OXFORD. [*Received, April 4th*, 1928.]

CCCXLII.—*Stereoisomerism in Polycyclic Systems. Part V.*

By WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON PLANT.

IT has been shown that although the reduction of tetrahydrocarbazole with tin and hydrochloric acid in aqueous alcohol leads almost entirely to the *cis*-modification of hexahydrocarbazole, the *trans*- being produced in only small amount (Gurney, Perkin, and Plant, J., 1927, 2676), yet the reduction of 2 : 3-dihydroquinindene under similar conditions gives relatively large quantities of both the *cis*- and the *trans*-form of 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene (Perkin and Plant, this vol., p. 639). These facts were found to be in accordance with the deductions which could be drawn from a consideration of the relative strains in the various multiplanar configurations. The present communication deals with an extension of these considerations to some systems containing seven-membered rings. Owing to the fact that the multiplanar *cyclo*heptane ring can pass by free rotation into a strainless phase in which the *trans* valencies of two neighbouring carbon atoms, when projected on to a plane at right angles to the line joining these two atoms, enclose only a very small angle, it appears that there



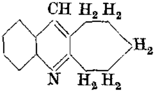
cis- (I.) *trans*- (II.) (III.)

should be relatively less strain in the *trans*-configuration of 2 : 3 : 4 : 5 : 11 : 12-*hexahydroheptindole* (II) than in *trans*-hexahydro-

carbazole. It was thought, therefore, that the reduction of 2 : 3 : 4 : *5-tetrahydroheptindole* * (III) with tin and hydrochloric acid in aqueous alcohol might lead to relatively large quantities of both the stereoisomeric hexahydro-derivatives (I) and (II).

2 : 3 : 4 : 5-Tetrahydroheptindole has been prepared by Fischer's indole synthesis from suberonephenylhydrazone, its reduction under the above conditions has been investigated, and the product has been found to consist almost entirely of a single form (presumably the *cis*-, since this is likely to be the less strained) of 2 : 3 : 4 : 5 : 11 : 12-hexahydroheptindole, not more than 5% of any stereoisomeride being present. This modification of hexahydroheptindole is basic, readily yielding a *picrate*, and *acetyl* and *benzoyl* derivatives. The isolation of the small quantity of the second form, which may possibly be present here as it was in the case of hexahydrocarbazole, was not attempted on account of the difficulty of obtaining the large amounts of suberone which would be required for such an investigation.

The results obtained in the above investigations suggested that a study of the reduction of 7 : 8 : 9 : 10-tetrahydroheptaquinoline † (IV) to 5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-octahydroheptaquinoline (V) would be interesting. In this instance, as in the case of octahydroacridine (Perkin and Sedgwick, J., 1924, **125**, 2437) and of 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene (VI) (Perkin and Plant, *loc. cit.*), there should be very little difference in the strains of the



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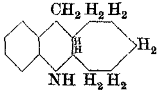

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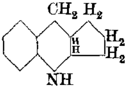
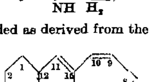


(VI.)

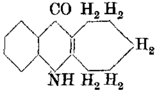
two stereoisomeric octahydro-derivatives, and relatively large quantities of the two forms should again be produced. We have pre-

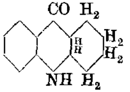
* This substance is regarded as derived from the hypothetical parent compound " heptindole,"



† This substance is regarded as derived from the hypothetical parent compound " heptaquinoline,"

ared 7 : 8 : 9 : 10-tetrahydroheptaquinoline by the elimination of arbon dioxide from 7 : 8 : 9 : 10-tetrahydroheptaquinoline-11-carb- xylic acid (compare Borsche, *Annalen*, 1910, **377**, 122), and have ound that on reduction by means of tin and hydrochloric acid in queous-alcoholic solution it yields an oily base. By benzoylation ee Experimental), this was shown to consist almost entirely of ne of the two possible forms of 5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-*octa- ydroheptaquinoline*, admixed with a small amount of the unreduced etrahydro-compound. The failure to isolate more than one tereoisomeride in these two reduced systems containing 7-membered ings is surprising and difficult to explain. Previous work in this eld has indicated that the constitution of the product is influenced y the nature of the reducing agent used and depends also upon the ature of the starting material. It was hoped, therefore, that the econd stereoisomeride of 5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-octahydro- eptaquinoline would result from the reduction of 11-*keto- : 7 : 8 : 9 : 10 : 11-hexahydroheptaquinoline* (VII) with sodium malgam. We have prepared this keto-derivative by condensing nthranilic acid with suberone, but have found that reduction under hese conditions and subsequent benzoylation of the oily product ields a single benzoyl derivative identical with that obtained by he previous method.

(VII.) 

 (VIII.)

In Part I of this series (J., 1924, **125**, 2437), the formation of he two stereoisomeric octahydroacridines (A, m. p. 82°, and B, ı. p. 72°) by the reduction of tetrahydroacridine with tin and ydrochloric acid in aqueous alcohol is described. The more recent evelopments of this work have made it desirable to determine the elative amounts of the two modifications produced under these onditions, and we have now found that the ratio of octahydro- cridine (A) to octahydroacridine (B) in the product is approximately to 4. The reduction of tetrahydroacridone with sodium amalgam ielded entirely octahydroacridine (A) (Perkin and Sedgwick, *loc. it.*), but it has been found during the course of the present work hat the action of tin and hydrochloric acid on tetrahydroacridone n aqueous alcohol is to give a small quantity of a base which appears o be one of the two possible *hexahydroacridones* (VIII). This struc- ure is confirmed by the fact that it gives an *oxime* (p. 2590).

EXPERIMENTAL.

2 : 3 : 4 : 5-*Tetrahydroheptindole*.—After equal weights of suberone and phenylhydrazine had been warmed together on the water-bath for 5 minutes and then cooled, the product solidified, and suberone phenylhydrazone could be obtained from dilute alcohol in colourless needles, m. p. 72°. When a mixture of the crude hydrazone (18 g.) water (360 c.c.), and concentrated sulphuric acid (20 c.c.) was heated on the water-bath for 25 minutes with frequent shaking, 2 : 3 : 4 : 5-*tetrahydroheptindole* (11 g.) gradually separated in a practically pure condition. On crystallisation from alcohol it was isolated in colourless plates, m. p. 144° (Found : N, 7·4. $C_{13}H_{15}N$ requires N, 7·6%). The *picrate* was obtained from hot alcohol in dark crimson plates, m. p. 142°.

2 : 3 : 4 : 5 : 11 : 12-*Hexahydroheptindole*.—A mixture of 2 : 3 : 4 : 5-tetrahydroheptindole (10 g.), alcohol (30 c.c.), granulated tin (30 g.), and concentrated hydrochloric acid (30 c.c.) was boiled under reflux for 5 hours, filtered, the tin residues washed with a little hot alcohol, and the alcohol distilled off from the united filtrates. After being made alkaline with a concentrated aqueous solution of sodium hydroxide (30 g.) and cooled, the whole was filtered through asbestos, and both the solid and the filtrate were extracted with ether. The solid residue then remaining was dissolved in dilute hydrochloric acid, the solution was made alkaline with aqueous sodium hydroxide and again extracted with ether. When the united ethereal solutions were dried over potassium carbonate and the solvent removed, the residue solidified on cooling. On crystallising from alcohol, 2 : 3 : 4 : 5 : 11 : 12-*hexahydroheptindole* (2·9 g.) separated in colourless plates, m. p. 77°, unaltered by further recrystallisation (Found : C, 83·4; H, 9·2. $C_{13}H_{17}N$ requires C, 83·4; H, 9·1%). After removal of the solvent from the alcoholic filtrate, the residue melted at 67—70°, and crystallisation of this from a small quantity of alcohol yielded a further quantity (3·3 g.) of the hexahydroheptindole, m. p. 72—74° (mixed m. p. 73—75°). The solvent was then again removed from the filtrate, and the residue extracted with dilute hydrochloric acid, which left a small quantity of a dark red, resinous material. After the acid solution had been made alkaline with ammonia, the base obtained (2·0 g., m. p. 45—55°) was treated in hot alcohol with picric acid (2·5 g.). The picrate (2·4 g., equivalent to 1·1 g. of base) which separated, m. p. 176° (decomp.), proved to be identical with the picrate of 2 : 3 : 4 : 5 : 11 : 12-hexahydroheptindole described below, and, on decomposition with aqueous sodium hydroxide, it yielded the base, m. p. 77°. The alcoholic filtrate from the picrate was shaken with ether and dilute aqueous sodium

hydroxide, and the ethereal solution extracted with dilute hydrochloric acid. The small amount (0·6 g.) of base obtained by making this acid solution alkaline with ammonia melted at 35—45°, and on benzoylation gave a product which, after crystallisation from methyl alcohol, yielded 0·2 g. of the benzoyl derivative described below. It is thus apparent that not more than a very small quantity of any second stereoisomeride can be present in the product of the reduction of 2 : 3 : 4 : 5-tetrahydroheptindole by the above method.

2 : 3 : 4 : 5 : 11 : 12-Hexahydroheptindole forms a sparingly soluble *hydrochloride*, but this dissolves in much water, and the base is reprecipitated by adding ammonia. When the product obtained by boiling a solution of the base in acetic anhydride for 15 minutes, cooling and shaking with water, was crystallised from dilute alcohol, *10-acetyl-2 : 3 : 4 : 5 : 11 : 12-hexahydroheptindole* was obtained in long, silky, colourless needles, m. p. 87° (Found : N, 6·3. $C_{15}H_{19}ON$ requires N, 6·1%). When the base was shaken with benzoyl chloride and aqueous sodium hydroxide, *10-benzoyl-2 : 3 : 4 : 5 : 11 : 12-hexahydroheptindole* resulted; it separated from alcohol in clusters of colourless prisms, m. p. 116° (Found : N, 4·9. $C_{20}H_{21}ON$ requires N, 4·8%). The *picrate* of the base was isolated from alcohol in yellow prisms, m. p. 176° (decomp.).

7-Bromo-2 : 3 : 4 : 5-tetrahydroheptindole.—When suberone (4 g.) and *p*-bromophenylhydrazine (6 g.) were mixed in a small quantity of hot alcohol, *suberone-*p*-bromophenylhydrazone* separated, on cooling, in colourless plates, m. p. 57°, which quickly decomposed on exposure to the air. The alcoholic mixture was added to water (500 c.c.) containing concentrated sulphuric acid (60 c.c.), and the whole was boiled for 10 minutes. The product separated as a dark red oil, which solidified on cooling, and, after crystallisation from alcohol, *7-bromo-2 : 3 : 4 : 5-tetrahydroheptindole* was obtained in colourless plates, m. p. 129—130° (Found : N, 5·5. $C_{13}H_{14}NBr$ requires N, 5·3%). It is not basic, being precipitated from its solution in concentrated sulphuric acid by pouring into water. The reduction of this substance by means of tin and hydrochloric acid in aqueous alcohol was studied, but partial debromination occurred during the process.

Reduction of 7 : 8 : 9 : 10-Tetrahydroheptaquinoline.—A mixture of 7 : 8 : 9 : 10-tetrahydroheptaquinoline (12 g., prepared from suberone and isatin as described by Borsche, *loc. cit.*), alcohol (60 c.c.), concentrated hydrochloric acid (60 c.c.), and granulated tin (60 g.) was boiled under reflux for 9 hours, a further quantity (20 c.c.) of hydrochloric acid being added after 5 hours. The liquid was then filtered, the solid residue washed with alcohol, and as much alcohol as possible removed by distillation from the united liquors. The

residue was made alkaline by the addition of a concentrated aqueous solution of sodium hydroxide (80 g.), and extracted several times with ether. After the extract had been dried over potassium carbonate and the solvent removed, the residual oil, which could not be made to solidify, was shaken with dilute aqueous sodium hydroxide and benzoyl chloride (15 g.). The solid product was dissolved in a considerable quantity of ether, the solution shaken with dilute hydrochloric acid, which removed a quantity (2·3 g., isolated by making the acid solution alkaline) of unreduced 7 : 8 : 9 : 10-tetrahydroheptaquinoline, dried over calcium chloride, and the solvent distilled off. The solid residue (13·3 g.) melted at 133—137°, and after crystallisation from alcohol, *5-benzoyl-5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-octahydroheptaquinoline* (9·3 g.) separated in colourless prisms, m. p. 145° (Found : C, 82·8; H, 7·6. $C_{21}H_{23}ON$ requires C, 82·6; H, 7·5%). By concentrating the alcoholic mother-liquor, a further quantity (1·1 g.) of the benzoyl compound was obtained, and it is clear that no appreciable quantity of a stereoisomeride of this benzoyl compound can be present.

5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-*Octahydroheptaquinoline*.—A solution of the benzoyl derivative (m. p. 145°) in aqueous-alcoholic potassium hydroxide was boiled for 24 hours, the alcohol removed, and the residue shaken with ether and water. The base was removed from the unchanged benzoyl compound, which was also present in the ether, by extraction with dilute hydrochloric acid, recovered by adding ammonia, and taken up in ether. 5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-*Octahydroheptaquinoline* was collected as a colourless oil, b. p. 203°/24 mm. (Found : C, 83·9; H, 9·2. $C_{14}H_{19}N$ requires C, 83·6; H, 9·4%). Its *picrate* separated from alcohol in orange-red prisms, m. p. 196°.

11-*Keto*-5 : 7 : 8 : 9 : 10 : 11-*hexahydroheptaquinoline*.—This substance was obtained by a process analogous to that used by Tiedtke (*Ber.*, 1909, **42**, 624) for the preparation of tetrahydroacridone. Anthranilic acid (3·5 g.) and suberone (4 c.c.) were heated together at 120° for an hour and then at 210° for 15 minutes. The solid was boiled for 1½ hours with benzene, in which it is sparingly soluble, collected, and crystallised from alcohol; *11-keto-5 : 7 : 8 : 9 : 10 : 11-hexahydroheptaquinoline* then separated in colourless plates, m. p. 344—345° (Found : N, 6·5. $C_{14}H_{15}ON$ requires N, 6·6%).

The keto-compound (6 g.), dissolved in boiling alcohol (300 c.c.) to which a little sodium bicarbonate had been added, was treated gradually at 80° with sodium amalgam (450 g. of 4%), the whole being vigorously stirred and carbon dioxide being passed continuously. After 6 hours, the mixture was filtered, the solid washed with alcohol, and the alcohol removed from the united filtrates

under reduced pressure. The residue was shaken with ether and water, the ether layer dried over potassium carbonate, and the solvent removed. After distilling under reduced pressure, the residual oil did not solidify, and, on shaking with benzoyl chloride (4·5 g.) and dilute aqueous sodium hydroxide, it yielded 5-benzoyl-5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-octahydroheptaquinoline, isolated from alcohol in colourless prisms, m. p. 145°. The mixture with the benzoyl compound obtained from the reduction product of 7 : 8 : 9 : 10-tetrahydroheptaquinoline also melted at 145°.

Reduction of Tetrahydroacridine with Tin and Aqueous-alcoholic Hydrochloric Acid.—A mixture of tetrahydroacridine (27 g.), alcohol (100 c.c.), concentrated hydrochloric acid (100 c.c.), and granulated tin (100 g.) was boiled under reflux for 5 hours, filtered, and the alcohol distilled off from the filtrate. The residue, after being made alkaline with sodium hydroxide (100 g. in concentrated aqueous solution), was extracted repeatedly with ether; from the extract, dried over potassium carbonate, a product was obtained which solidified on cooling and was crystallised from petroleum (b. p. 40—60°). Octahydroacridine (B) (6·7 g.) separated, and a further quantity (3·0 g.) was obtained by concentrating the mother-liquor. The petroleum was then completely removed, the residue heated to boiling for ½ hour with an excess of acetic anhydride, and the whole shaken with water (1500 c.c.) and left for several hours. The solid product was extracted with ether, and from the aqueous layer a small quantity (1·3 g.) of unchanged tetrahydroacridine was obtained by making it alkaline with ammonia and extracting it with ether. The extract containing the acetyl derivatives was shaken with dilute aqueous sodium carbonate, dried over calcium chloride, the solvent removed, and the residue crystallised from alcohol, 10-acetyloctahydroacridine (B) (7·0 g., m. p. 135—136°) being thus obtained; by distilling off the alcohol from the mother-liquor and crystallising the product from petroleum (b. p. 60—80°), a further quantity (1·7 g.) of the same substance was collected. After the mother-liquor was again evaporated to dryness, the residue was treated with potassium hydroxide (25 g.) in aqueous alcohol, and the whole boiled for 24 hours. The mixture, after removal of the alcohol, was diluted with water and shaken with ether; the ethereal layer was extracted with dilute hydrochloric acid and then evaporated, and the fact that no appreciable residue remained indicated complete hydrolysis of the acetyl derivatives. The aqueous acid solution was made alkaline with ammonia, and the basic product taken up in ether and dried with potassium carbonate. After removal of the ether, the residue (7·2 g.) solidified. It was dissolved in alcohol and treated with an alcoholic solution of picric acid (10 g.), whereupon the picrate of

octahydroacridine (A) (10·5 g., m. p. 198°) rapidly separated: the free (A) base was obtained from this by treatment with dilute aqueous sodium hydroxide and extraction with ether. The product remaining in the mother-liquor after removal of the picrate was clearly small and was essentially the picrate of octahydroacridine (B), for when the liquid was shaken with aqueous sodium hydroxide and ether, and the extracted base was crystallised from petroleum, octahydroacridine (B) (0·5 g., m. p. 72°) separated. The identities of the substances isolated were definitely established by mixed m. p. determinations with the products obtained as described by Perkin and Sedgwick (*loc. cit.*); the total amounts correspond to 17·3 g. of octahydroacridine (B) and 4·7 g. of octahydroacridine (A).

Hexahydroacridone.—A mixture of tetrahydroacridone (12 g.), alcohol (70 c.c.), concentrated hydrochloric acid (70 c.c.), and granulated tin (70 g.) was boiled for 6 hours, filtered, the alcohol removed, and the residue made alkaline with sodium hydroxide (70 g. in concentrated aqueous solution). After extraction with ether, drying with potassium carbonate, and removal of the solvent, the small quantity (about 0·5 g.) of solid obtained was crystallised from alcohol, from which *hexahydroacridone* separated in yellow plates, m. p. 180° (Found: C, 77·4; H, 7·7. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5%). The unreduced tetrahydroacridone was recovered by acidifying the mixture after the ether extraction with concentrated hydrochloric acid, collecting the hydrochloride, dissolving this in much water, and adding concentrated nitric acid. The nitrate of tetrahydroacridone gradually separated in a pure condition, and the free base was obtained from this with sodium hydroxide.

Hexahydroacridone, which is readily soluble in dilute hydrochloric acid, was treated in alcoholic solution with hydroxylamine hydrochloride and sodium acetate, the mixture boiled for 2 hours, the alcohol distilled off, and the residue shaken with water. The *oxime* separated from alcohol in pale yellow prisms, m. p. 215—216° (Found: N, 13·1. $C_{13}H_{16}ON_2$ requires N, 13·0%).

The authors wish to express their gratitude to Professor J. F. Thorpe for his gift of the suberone used in this work, and one of them (S. G. P. P.) wishes gratefully to acknowledge the receipt of a grant from the Chemical Society Research Fund, which has defrayed a part of the cost of this investigation.

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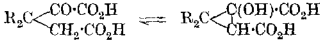
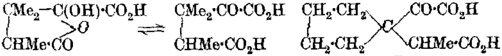
CCCXLIII.—*Experiments on the Synthesis of Certain γ-Ketonic Acids Closely Allied to Balbiano's Acid. Part I. Synthesis of α-Methyl*cyclo*pentane-1 : 1-diacetic Acid, of the Lactone of α-Hydroxy-α-methyl*cyclo*pentane-1 : 1-diacetic Acid, and of 1-Acetyl*cyclo*pentane-1-acetic Acid.*

By JOGENDRA CHANDRA BARDHAN.

THE outcome of work which has been carried out in these laboratories during the past few years has been to show that in certain ββ-disubstituted ketoglutaric acids there exists a kind of tautomerism (keto-cyclol type) between the open-chain keto-form (I) and the hydroxy-ring form (II) (compare, *e.g.*, Deshapande and Thorpe, J., 1922, **121**, 1430; Bains and Thorpe, J., 1923, **123**, 1206). In

(I.)  (II.)

the case of the corresponding acids containing an additional α-substituent, however, other factors come into play which considerably reduce the tendency to *cyclo*propane ring formation. The determining conditions are well illustrated in the case of an acid $C_8H_{12}O_5$ (Balbiano's acid), which has recently been dealt with by Kon, Stevenson, and Thorpe (J., 1922, **121**, 650), by Pandya and Thorpe (J., 1923, **123**, 2825), and by Rothstein, Stevenson, and Thorpe (J., 1925, **127**, 1072). Here, the usual keto-cyclol change is completely suspended, the substance exhibiting a marked tendency to pass into the lactol-form (III), which in the liquid state or in solution comes into equilibrium with the tautomeric parent (IV).



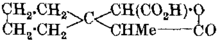
(III.) (IV.) (V.)

In view of the light which this phenomenon throws on the difficult question of the constitution of Balbiano's acid, it seemed desirable to ascertain the rôle played by the α-substituent, and, incidentally, to synthesise other keto-acids capable of exhibiting this kind of tautomerism.

In the course of an extended series of investigations on *spiro*- and associated alicyclic compounds, Thorpe and his co-workers have shown that the angle of the *cyclo*pentane ring is very close to that included between the *gem*-dimethyl groupings (Becker and Thorpe, J., 1920, **117**, 1579; Dickens, Kon, and Thorpe, J., 1922,

121, 1496; Lanfear and Thorpe, J., 1923, **123**, 1683; Ingold, Lanfear, and Thorpe, *ibid.*, p. 3140). It is to be expected, therefore, that the acid (V) would, if it could be synthesised, simulate the characteristic properties of Balbiano's acid. A general method of synthesis of α-ketoglutaric acids, indicated many years ago by Perkin and Thorpe (J., 1901, **79**, 737), consists in converting a substituted glutaric acid by means of the Hell–Volhard method into the dibromo-ester, from which the keto-acid is obtained either directly through the action of alkali or by further hydrolysis of the intermediate *cyclo*propane compounds through the agency of concentrated hydrobromic acid. Unfortunately, the above reaction breaks down in the case of the corresponding glutaric acids containing an additional α-substituent, owing to the occurrence of an abnormal decomposition, whereby the dibromo-ester is transformed into oxalic acid and an acid of the acrylic series (compare Pandya and Thorpe, *loc. cit.*, p. 2855; also Kon, Smith, and Thorpe, J., 1925, **127**, 567).

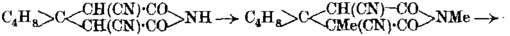
The necessity therefore arose of devising methods for the synthesis of αββ-trisubstituted ketoglutaric acids. A consideration of the conditions under which Balbiano's acid is produced showed that the synthesis of the *cyclo*pentane acid (V) might be attained through the oxidation of (i) the lactonic acid (VI) and (ii) the *spiro*-compound (VII) by means of alkaline permanganate, and a number of experi-


(VI.)

(VII.)

ments were made with this end in view. Although these attempts were unsuccessful, the results obtained led to the isolation of a number of substances of considerable interest.

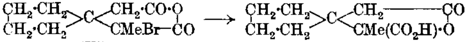
The starting point in these attempts was *α-methyl*cyclo*pentane-1 : 1-diacetic acid* (X), which was prepared in quantity by methylating the imide (VIII) and hydrolysing the resulting *methylimide* (IX) with mineral acid. The *anhydride* of the acid (X) on treatment


(VIII.) (IX.)

(X.)

with the calculated amount of bromine gave a monobromo-compound (XI), which on hydrolysis with alkali readily furnished a crystalline lactonic *acid* (XII). This acid is very resistant to oxidising and reducing agents, and in this respect resembles the corresponding

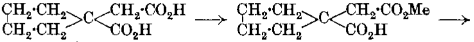
gem-dimethyl lactonic acid prepared by Blanc (*Bull. Soc. chim.*, 1901, **25**, 68).



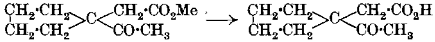
(XI.) (XII.)

That the above scheme correctly represents the course of the bromination follows from the following synthesis of the lactonic acid (XII), which leaves no room for doubt as to its constitution.

1-*Acetyl*cyclo*pentane*-1-*acetic acid* (XVI) was first prepared in the following manner: *cyclo*Pentane-1-acetic-1-carboxylic acid (XIII), prepared by an extension of Lapworth and McRae's method (J., 1922, **121**, 2754), was successively converted into its *anhydride* and acid *ester* (XIV); the *acid chloride* of this ester was then allowed to react with zinc methyl iodide to give a product (XV), which on hydrolysis yielded 1-acetyl*cyclo*pentane-1-acetic acid.

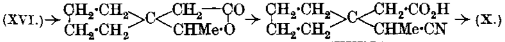


(XIII.) (XIV.)



(XV.) (XVI.)

This synthesis, although simple and convenient as a method of preparation, does not provide an adequate basis for the constitution assigned to the acid (XVI), since the acid ester (XIV) might have an alternative structure. To settle this point, the keto-acid (XVI) was reduced with sodium and alcohol, the lactone (XVII) was converted by potassium cyanide into the cyano-compound (XVIII), and hydrolysis then yielded the acid (X), the identity of which was established by direct comparison.

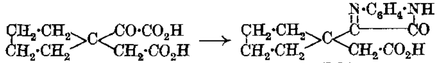


(XVII.) (XVIII.)

1-Acetyl*cyclo*pentane-1-acetic acid shows all the properties of a ketonic acid; its *methyl* ester readily yields a *semicarbazone* and in this respect differs from its *cyclo*hexane analogue (Rothstein and Thorpe, J., 1926, 2014).

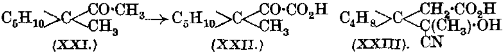
On oxidation with alkaline permanganate at the ordinary temperature the ketonic ester (XV) yielded an acid (XIX) which gave a condensation product (XX) with *o*-phenylenediamine. Although no authentic material was available for comparison, there can be no doubt that the acid is α-keto*cyclo*pentane-1 : 1-diacetic acid, previously obtained by Lanfear and Thorpe (J., 1923, **123**, 1688)

by the hydrolysis of the dibromo-ester of *cyclo*pentane-1 : 1-diacetic acid. Its formation in the present instance must have been due to



(XIX.) (XX.)

the oxidation of the methyl group, the reaction being precisely similar to the oxidation of the *cyclo*hexane ketone (XXI), which gives the keto-acid (XXII) as the sole product (Tarbourisch, *Compt. rend.*, 1910, **150**, 1606).



(XXI.) (XXII.) (XXIII).

The above reaction is very important, as it opens up a possibility of synthesising α-ketoglutaric acids, the preparation of which by the more obvious synthetical methods is either difficult or impossible. There can be no doubt, moreover, that the formation of trimethylpyruvic acid from pinacolin (Glucksmann, *Monatsh.*, 1889, **10**, 771) and of benzoylformic acid from acetophenone (Claus and Neukranz, *J. pr. Chem.*, 1891, **44**, 777) are instances of a very general reaction whereby an acetyl group attached to a quaternary carbon atom is similarly transformed into the corresponding oxalyl derivative.

In order to obtain the lactonic acid (XII), 1-acetyl*cyclo*pentane-1-acetic acid (XVI) was allowed to react with hydrocyanic acid, and under the prescribed conditions (p. 2602) combination readily took place with the formation of (XXIII), which on hydrolysis smoothly passed into the desired lactonic acid, which proved to be identical in all essential respects with that obtained in the bromination of α-methyl*cyclo*pentane-1 : 1-diacetic acid.

It therefore follows that in the bromination of the acid (X), the bromine atom has entered the carbon atom adjacent to the methyl group. It is somewhat remarkable that no trace of the isomeric bromo-derivative could be obtained, although Pandya and Thorpe (*loc. cit.*) succeeded in isolating both the possible lactonic acids from the products of the bromination of αββ-trimethylglutaric acid. On the other hand, Hariharan, Menon, and Simonsen (this vol., p. 432) obtained only one lactonic acid from the action of alkali on the monobromo-derivative of α-*iso*propylglutaric acid.

In order to avoid the formation of the lactonic acid (XII), it was next decided to brominate the monoethyl ester (prepared by partial hydrolysis of the normal ester) of α-methyl*cyclo*pentane-1 : 1-diacetic acid (XXIV), for in this case only the bromo-ester (XXV) could be formed, and on hydrolysis this should yield the desired

lactonic acid (VI). The bromination did not proceed very smoothly, however, and the crude product on treatment with alkali yielded a

$$C_4H_8{>}C{<}\begin{matrix}CH_2\cdot CO_2H\\ CHMe\cdot CO_2Et\end{matrix} \longrightarrow C_4H_8{>}C{<}\begin{matrix}CHBr\cdot CO_2Et\\ CHMe\cdot CO_2Et\end{matrix}$$

(XXIV.) (XXV.)

gummy acid from which no material of any definite composition could be obtained. On one occasion the impure acid was oxidised with alkaline permanganate and the resulting product was treated with *o*-phenylenediamine, but no trace of any quinoxaline derivative indicating the formation of the keto-acid (V) could be detected.

Finally, an attempt was made to prepare the lactonic acid (VI) by the hydrolysis of the *bromo*-compound (XXVI), which was readily prepared by direct bromination of the imide (IX); but on hydrolysis with concentrated hydrochloric acid the substance apparently lost bromine, the only isolable product being the acid (X), evidently derived from the original imide.

$$\text{(XXVI.)}\quad \begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{<}\begin{matrix}CBr(CN)-CO\\ CMe(CN)\cdot CO\end{matrix}{>}NMe$$

Several preliminary experiments have also been made with a view to synthesise the *cyclo*pentane analogue of camphoric acid (VII) by an extension of Komppa's method (*Annalen*, 1909, **370**, 209; **368**, 126), but these, together with a much easier method of preparing α-ketoglutaric acids which has now been discovered, are reserved for future communications.

During preliminary attempts to obtain the acid (X), a *ketone* was prepared from the acid (XXVII) (Wallach and Martins, *Annalen*, 1909, **365**, 272) by means of the Blaise reaction, and might therefore be expected to possess the αβ-structure (XXVIII). It readily yielded a mixture of two *semicarbazones*, one melting at 189° and the other at 169°; the regenerated ketones showed identical physical properties, and an exaltation characteristic of αβ-unsaturated ketones. Moreover, the corresponding *βγ-ketone* (XXX),

$$\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{:}CMe\cdot CO_2H \longrightarrow \begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{:}CMe\cdot COMe$$

(XXVII.) (XXVIII.)

$$\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}{\gg}C\cdot CHMe\cdot CO_2H \longrightarrow \begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}{\gg}C\cdot CHMe\cdot COMe$$

(XXIX.) (XXX.)

prepared from the acid (XXIX) (Wallach and Martins, *loc. cit.*, p. 271), gave a *semicarbazone* melting at 144°, and was markedly different from the αβ-ketones in physical properties. It seems probable that the semicarbazones are stereoisomeric like those of mesityl oxide (Wilson and Heilbron, J., 1913, **103**, 378). It is

proposed to investigate the action of ultra-violet light on these semicarbazones with a view to determine whether and under what conditions they may be interconvertible.

EXPERIMENTAL.

A. *Synthesis of* α-*Methyl*cyclo*pentane*-1 : 1-*diacetic Acid* (X).

The imide of αα′-dicyanocyclopentane-1 : 1-diacetic acid was prepared by condensing cyclopentanone with cyanoacetic ester and alcoholic ammonia (Kon, J., 1921, **119**, 818; Kon and Thorpe, J. 1919, **115**, 686). The crude product (yield 60%), after having been dried in the steam-oven, was directly used in the experiment described below.

N-*Methyl*-ω-*imide of* αα′-*Dicyano*-α-*methyl*cyclo*pentane*-1 : 1-*diacetic Acid* (IX).—In the preparation of this substance by an extension of Kon and Thorpe's method (J., 1922, **121**, 1795), it was found essential to adhere to the following conditions: The above imide (108 g.), dissolved in absolute alcohol (300 c.c.), was gradually added with vigorous shaking to a solution of sodium ethoxide prepared from sodium (35 g.) and absolute alcohol (500 c.c.); the biscuit-coloured sodium salt which separated was cooled in ice, cautiously mixed with methyl iodide (100 c.c.), and the mixture allowed slowly to attain room temperature. After 12 hours, the clear solution was heated under reflux on the steam-bath until neutral. The greater part of the alcohol was then evaporated off, the residue mixed with water (2 l.), and slightly acidified with hydrochloric acid. The methylated imide which separated as a viscous gum was washed with hot water, and when left in contact with methylated spirit gradually solidified to a brittle resin. This was thoroughly ground in a mortar with alcohol and the solid collected, washed successively with sodium sulphite solution, water, and alcohol, and dried. The material (90 g.), m. p. 132—135°, is sufficiently pure for most purposes, but can be recrystallised from alcohol, from which it separates as minute, colourless prisms, m. p. 136—137° (Found: C, 63·6; H, 6·2; N, 17·4. $C_{13}H_{15}O_2N_3$ requires C, 63·7; H, 6·1; N, 17·1%). The *imide* slowly dissolves in alkali and is reprecipitated on the addition of dilute acids.

Hydrolysis of the Methylated Imide: Formation of α-*Methyl*cyclo*pentane*-1 : 1-*diacetic Acid*.—(i) *With sulphuric acid.* The imide (87 g.) was dissolved in sulphuric acid (400 c.c.; *d* 1·84), and after remaining over-night, the viscous liquid was cautiously mixed with water (365 c.c.) and boiled under reflux for 8—10 hours. The solution was cooled, diluted with water, saturated with ammonium sulphate, and exhaustively extracted with ether. The ethereal extract was washed with a moderately concentrated solution

sodium carbonate, from which the acid (55 g.) was recovered in the usual way as a pale yellow oil which rapidly solidified when kept in an evacuated desiccator over sulphuric acid. The residue from the ethereal extract above consisted of a neutral liquid which partly solidified on keeping. The solid product on purification first from alcohol and then from glacial acetic acid was obtained in pearly plates, m. p. 223—224° (Found: C, 59·1; H, 6·1; N, 11·0. $C_{13}H_{16}O_4N_2$ requires C, 59·1; H, 6·1; N, 10·7%). Owing to the small amount available, the constitution of this *substance* could not be determined.

(ii) *With hydrochloric acid.* The imide (5 g.) was heated with concentrated hydrochloric acid (35 c.c.) at 160—180° in a closed tube for 5 hours, and the acid was isolated in the usual way in nearly quantitative yield and of a high degree of purity.

*α-Methyl*cyclo*pentane*-1 : 1-*diacetic acid* crystallises from benzene–light petroleum (b. p. 40—60°) in small, colourless prisms, m. p. 90—91° (Found: C, 60·0; H, 8·1; *M*, 200·2. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%; *M*, 200), readily soluble in acetone, alcohol, ethyl acetate, and ether, moderately soluble in benzene and water, and almost insoluble in hydrochloric acid and light petroleum. A neutral solution of the ammonium salt of the acid gives a bluish-green, crystalline precipitate with copper acetate, a white, crystalline precipitate on boiling with calcium chloride, and a heavy white precipitate with lead acetate. The *silver* salt, prepared in the usual manner, is a white, curdy, insoluble precipitate (Found: Ag, 51·9. $C_{10}H_{14}O_4Ag_2$ requires Ag, 52·2%).

The *anhydride*, prepared by boiling with excess of acetic anhydride, distils at 193°/24 mm. as a colourless liquid, and solidifies to a crystalline cake on cooling. It crystallises from light petroleum (b. p. 40—60°) and chloroform in colourless transparent plates, m. p. 48° (Found: C, 65·9; H, 7·7. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·7%), and dissolves in aqueous alkali when warmed, the acid (m. p. 90—91°) being deposited on acidification of the solution.

The *β-naphthylamic acid*,

$$C_{10}H_7{\cdot}NH{\cdot}CO{\cdot}CHMe{\cdot}C(\dot{}C_4H_8){\cdot}CH_2{\cdot}CO_2H \ (?),$$

prepared from the anhydride, was obtained as a viscid oil, which solidified in contact with methyl alcohol and separated on recrystallisation in microscopic needles, m. p. 133—134° (Found: C, 73·9; H, 7·4. $C_{20}H_{23}O_3N$ requires C, 73·7; H, 7·1%). The corresponding derivatives of aniline and *p*-toluidine could only be obtained as oils.

The *β-naphthylimide*, obtained by heating the naphthylamic acid to 180° in a test-tube and cooling, was twice crystallised from dilute alcohol (charcoal), and separated in colourless, glistening plates,

m. p. 179° (Found: C, 78·3; H, 6·9. $C_{20}H_{21}O_2N$ requires C, 78·2; H, 6·8%). The *imide*, obtained on heating the dried ammonium salt of the acid in a sealed tube at 150° for 4 hours (Thorpe and Young. J., 1903, **83**, 358), crystallises from boiling water (charcoal) in long, colourless needles, m. p. 123—124° (Found: C, 66·7; H, 8·3; N, 7·9. $C_{10}H_{15}O_2N$ requires C, 66·3; H, 8·3; N, 7·7%); on boiling with a 30% solution of sulphuric acid, it was rapidly hydrolysed, and on extraction of the product with ether, the acid (m. p. 90—91°) was obtained in almost theoretical yield.

B. *Attempts to prepare the Lactone of α-Hydroxy-α′-methyl*cyclo*pentane*-1 : 1-*diacetic Acid* (VI).

*Bromination of α-Methyl*cyclo*pentane*-1 : 1-*diacetic Acid*.—Since the Hell–Volhard method did not give satisfactory results, the bromination was carried out as follows: The anhydride (6 g.) was treated with the calculated amount of bromine (5·3 g.) and heated in a sealed tube in a boiling water-bath for 5 hours; the liquid was then kept in a desiccator over potash to remove the last traces of hydrobromic acid. The resinous product was dissolved in light petroleum (b. p. 40—60°), and the solution cooled in a freezing mixture. The *bromo-anhydride* (XI) separated in colourless prisms, m. p. 95° (Found: Br, 30·1. $C_{10}H_{13}O_3Br$ requires Br, 30·7%).

Hydrolysis. The crude bromination product was boiled with an excess of 2*N*-sodium carbonate for 10 hours, the solution concentrated, acidified with concentrated hydrochloric acid, and evaporated to dryness, and the residue extracted with ethyl acetate. On removal of the solvent, a thick syrup was obtained which, when kept over sulphuric acid in a vacuum desiccator, began to crystallise. In contact with porous porcelain the mother-liquor was slowly absorbed, and a colourless crystalline residue of the *lactone* of *α-hydroxy-α-methyl*cyclo*pentane*-1 : 1-*diacetic acid* remained; it crystallised from ethyl acetate–light petroleum (b. p. 60—80°) (charcoal) in long, colourless needles, m. p. 140° (Found: C, 60·6; H, 7·0. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%), readily soluble in acetone, chloroform, and ethyl acetate, moderately soluble in benzene, and almost insoluble in light petroleum.

The *silver* salt was obtained from the ammonium salt as a rather soluble, white precipitate (Found: Ag, 35·7. $C_{10}H_{13}O_4Ag$ requires Ag, 35·4%). The *barium* salt, prepared from the lactonic acid by shaking with a suspension of barium carbonate, separated from a fairly concentrated solution in leaflets, which were dried at 110° [Found: Ba, 25·4. $(C_{10}H_{13}O_4)_2Ba$ requires Ba, 25·8%]. The *lead* salt is very soluble. The *ethyl* ester, obtained by saturating an alcoholic solution of the lactonic acid with hydrogen chloride, is a

mobile liquid, b. p. 197°/30 mm. (Found: C, 63·6; H, 8·2. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%).

*Bromination of Ethyl Hydrogen α-Methyl*cyclo*pentane*-1 : 1-*diacetate* (XXIV).—The *diethyl* ester, prepared by the esterification of the acid with alcohol and sulphuric acid, was obtained as a colourless oil, b. p. 165°/25 mm. (Found: C, 65·8; H, 9·3. $C_{14}H_{24}O_4$ requires C, 65·6; H, 9·4%). This was partly saponified as follows: The ester (25·6 g.) was boiled under reflux with potassium hydroxide (5·6 g.) in alcohol (30 c.c.) for ½ hour, the alcohol evaporated, the residue mixed with water, extracted with ether to remove any neutral product, and the aqueous solution acidified and again extracted with ether. The residual oil was kept in a vacuum desiccator for 2 days. The *silver* salt was obtained as a white precipitate (Found: Ag, 31·8. $C_{12}H_{19}O_4Ag$ requires Ag, 32·2%). The acid ester was warmed with excess of thionyl chloride for ½ hour, and the excess was removed under reduced pressure. The residue was mixed with the required amount of bromine and gently warmed (55°) until all the bromine had disappeared. It was then poured into an excess of ice-cold alcohol, and the mixture allowed to remain over-night. The product, *ethyl α-bromo-α'-methyl*cyclo*pentane*-1 : 1-*diacetate* (XXV), was then collected in ether after the addition of water. The residual oil was dried in a vacuum (Found: Br, 18·2. $C_{14}H_{23}O_4Br$ requires Br, 23·9%). The crude product was hydrolysed by boiling with an aqueous solution of sodium carbonate as described before. The brown oil did not show any tendency to solidify and all attempts to purify the product were fruitless. The oil was oxidised with alkaline permanganate and the resulting product warmed in acetic acid solution with an excess of *o*-phenylenediamine, but no quinoxaline derivative could be isolated.

Bromination of the Methylimide (IX).—A suspension of the methylimide in water was shaken with a slight excess of bromine for 24 hours (compare Gupta and Thorpe, J., 1922, **121**, 1900). The solid *methylimide* of *α-bromo-αα'-dicyano-α'-methyl*cyclo*pentane*-1 : 1-*diacetic acid* (XXVI), when collected and purified from alcohol, separated in colourless needles, m. p. 180° (decomp.) (Found: Br, 24·0. $C_{13}H_{14}O_2N_3Br$ requires Br, 24·7%). Hydrolysis with concentrated hydrochloric acid led to α-methyl*cyclo*pentane-1 : 1-diacetic acid, identified by its m. p. (90—91°) and by direct comparison with a known specimen.

C. *Synthesis of* 1-*Acetyl*cyclo*pentane*-1-*acetic Acid* (XVI) *and of the Lactone of α-Hydroxy-α-methyl*cyclo*pentane*-1 : 1-*diacetic Acid* (XII).

cyclo*Pentane*-1-*acetic*-1-*carboxylic Acid*.—This substance is obtained in excellent yield by the action of potassium cyanide on

ethyl *cyclo*pentylidenecyanoacetate (Harding and Haworth, J., 1910, **97**, 486) under the following conditions (compare Lapworth and McRae, *loc. cit.*). The ester (165 g.) was dissolved in rectified spirit (825 c.c.) to which was added a solution of potassium cyanide (115 g.) in water (260 c.c.). The clear solution was then allowed to stand at the ordinary temperature for about a week, during which a considerable amount of the potassium salt of the condensation product gradually separated. The mixture was evaporated on the steam-bath, and the dark residue then boiled with a large excess of concentrated hydrochloric acid for 6 hours. The solution was cooled and repeatedly extracted with ether, the extract dried, and the solvent removed. The residue of almost colourless solid (120 g.) consisted of nearly pure *cyclo*pentane-1-acetic-1-carboxylic acid, m. p. 156—156·5° (compare Norris and Thorpe, J., 1921, **119**, 1207) (Found: C, 55·8; H, 7·1. Calc.: C, 55·8; H, 7·0%). The *anhydride*, obtained by boiling the acid with acetyl chloride for 2 hours and fractionating under reduced pressure, was a colourless oil, b. p. 154°/20 mm., but it solidified in a freezing mixture and then had m. p. 30° (Found: C, 62·5; H, 6·6. $C_8H_{10}O_3$ requires C, 62·3; H, 6·5%). The *anilic acid*, prepared by mixing cold benzene solutions of the anhydride and aniline and crystallising the precipitated product from 84% alcohol, forms colourless plates, m. p. 167—167·5° (Found: C, 67·5; H, 6·8. $C_{14}H_{17}O_3N$ requires C, 68·0; H, 6·9%). The *anil*, prepared by heating the anilic acid, crystallises from alcohol in glistening prisms, m. p. 127—128° (Found: C, 73·4; H, 6·8. $C_{14}H_{15}O_2N$ requires C, 73·4; H, 6·6%). The *monomethyl* ester (XIV) was obtained by boiling the anhydride (46·2 g.) with methyl alcohol (24·4 c.c.) under reflux for 3 hours, removing excess of methyl alcohol in a vacuum, and crystallising the residue from light petroleum (b. p. 60—80°); it separated as magnificent transparent needles, m. p. 80—81° (Found: C, 58·0; H, 7·5; *M*, 185·5. $C_9H_{14}O_4$ requires C, 58·1; H, 7·5%; *M*, 186). The corresponding acid ethyl ester could not be solidified. The *acid chloride* was prepared by heating the acid ester (38 g.) with freshly distilled thionyl chloride (25 c.c.) at 50—60° in a glycerol-bath for 45 minutes; the excess of thionyl chloride was then removed in a vacuum, and the residue distilled under reduced pressure, giving a colourless oil, b. p. 132°/16 mm. The p-*toluidide* crystallises from dilute methyl alcohol in feathery needles, m. p. 111° (Found: C, 69·6; H, 7·6. $C_{16}H_{21}O_3N$ requires C, 69·8; H, 7·6%).

1-*Acetyl*cyclo*pentane*-1-*acetic Acid* (XVI).—The acid chloride described above was diluted with its own volume of dry benzene and gradually added during ¾ hour to a well-cooled solution of zinc methyl iodide prepared from zinc–copper couple (60 g.), methyl

iodide (25 c.c.), benzene (22 c.c.), and dry ethyl acetate (15 c.c.). After standing for an hour, the product was mixed with ice-cold dilute sulphuric acid, the benzene layer removed, washed successively with a 10% solution of potash, saturated ammonium sulphate solution, and water, dried, and distilled. The keto-ester boiled constantly at 121°/9 mm. as a colourless oil haviug a characteristic ethereal smell, but was uot sufficiently pure for analysis; it was therefore hydrolysed to the acid by boiling with alcoholic potash, and this was converted iuto the spariugly soluble *semicarbazone*, which crystallised from boiling water in long, colourless needles, m. p. 197° (Found: C, 53·3; H, 7·8. $C_{10}H_{17}O_3N_3$ requires C, 52·9; H, 7·5%).

The semicarbazone was gently warmed with dilute hydrochloric acid, the solution extracted with ether, the extract dried with sodium sulphate, and evaporated; the solid residue was recrystallised from light petroleum (b. p. 60—80°) and 1-*acetyl*cyclo*pentane*-1-*acetic acid* was thus obtained in shining plates, m. p. 83—84° (Found: C, 63·5; H, 8·1; *M*, 171. $C_9H_{14}O_3$ *requires* C, 63·5; H, 8·2%; *M*, 170). The keto-acid, on oxidation with sodium hypobromite, gave an excellent yield of *cyclo*pentane-1-acetic-1-carboxylic acid. The *oxime* crystallised from water in flat needles, m. p. 124—125° (Found: C, 58·2; H, 8·2. $C_9H_{15}O_3N$ requires C, 58·4; H, 8·1%). The *methyl* ester, prepared from the acid in the usual way, was obtained as an oil, b. p. 131°/18 mm. (Found: C, 65·0; H, 8·9. $C_{10}H_{16}O_3$ requires C, 65·3; H, 8·7%); it readily yielded a *semicarbazone*, which separated from alcohol in shining scales, m. p. 152—153° (Found: C, 54·7; H, 7·8. $C_{11}H_{19}O_3N_3$ requires C, 54·8; H, 7·9%). On treatment with dry sodium methoxide (Rothstein and Thorpe, *loc. cit.*, p. 2016), the ester was transformed into a gummy product which readily dissolved in dilute alkali and gave a brownish-violet colour with an aqueous-alcoholic solution of ferric chloride. The substance could not, however, be ohtained in a crystalline condition.

Reduction of 1-*Acetyl*cyclo*pentane*-1-*acetic Acid*.—Attempts to reduce the acid by means of sodium amalgam and by hydrogen in presence of platinum-black were unsuccessful, but reduction was ultimately effected as follows: The acid (5 g.) was dissolved in ethyl alcohol (15 c.c.), and sodium (4 g.) introduced in small lumps. The mixture was then heated at 112°, and alcohol (45 c.c.) gradually added during 2 hours. As soon as the last portions of sodium had disappeared, the excess of alcohol was removed in steam, the aqueous solution acidified, extracted with ether, the extract washed with sodium carbonate, dried, and evaporated. The *lactone* (XVII) was obtained on distillation under reduced pressure as a colourless oil, b. p. 132°/15 mm., having a characteristic smell

(Found : C, 69·6; H, 9·0. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1%); $d_{4°}^{15·8°}$ 1·057645, $n_D^{15·8°}$ 1·4742, $[R_L]_D$ 40·9 (calc., 41·0).

*Conversion of the Lactone into α-Methyl*cyclo*pentane*-1 : 1-*diacetic Acid.*—The lactone (5 g.) was heated with finely powdered 98% potassium cyanide (2·7 g.) in a sealed tube at 260° for 8 hours, and the resulting product acidified and repeatedly extracted with ether; the acidic product was washed out with an aqueous solution of sodium carbonate, and the alkaline solution evaporated to dryness. The residue was then boiled with an excess of 40% sulphuric acid for 3 hours; the acid isolated in the usual way melted at 90—91° and was identified as α-methyl*cyclo*pentane-1 : 1-diacetic acid by direct comparison and by the analysis of the silver salt (Found : Ag, 51·8. Calc. : Ag, 52·2%).

Oxidation of Methyl 1-*Acetyl*cyclo*pentane*-1-*acetate with Alkaline Permanganate : Formation of α-Keto*cyclo*pentane*-1 : 1-*diacetic Acid* (XIX).—The crude ester (6 g.) was stirred with water (400 c.c.), and to this was gradually added during 6 hours a solution of potassium permanganate (11 g.) and sodium hydroxide (4 g.) in 350 c.c. of water. The colour of the permanganate was slowly discharged, and after remaining for 12 hours, the solution became almost colourless. The filtrate and washings from the manganese precipitate were evaporated to small bulk, again filtered, and acidified with dilute hydrochloric acid. The liberated organic acids were dissolved in ether, and the semi-solid mass which remained on removal of the solvent was dissolved in glacial acetic acid, mixed with an excess of *o*-phenylenediamine, and slowly heated on the steam-bath for ½ hour. Excess of acetic acid was then removed, and the residue mixed with water. The brown, resinous product was collected and freed from impurities by rubbing with ether. The remaining solid was purified by two crystallisations from dilute acetone and thus obtained as a microcrystalline powder, m. p. 221° (Found : C, 66·3; H, 6·4. Calc. : C, 66·2; H, 5·9%). There can be no doubt, therefore, that the product consists of the quinoxaline derivative of α-keto*cyclo*pentane-1 : 1-diacetic acid (Lanfear and Thorpe, *loc. cit.*, p. 1688, give m. p. 222°).

Action of Hydrocyanic Acid on 1-*Acetyl*cyclo*pentane*-1-*acetic Acid : Synthesis of the Lactone of α-Hydroxy-α-methyl*cyclo*pentane*-1 : 1-*diacetic Acid* (XII).—The keto-acid (10 g.) was mixed with water (25 c.c.), and pure potassium cyanide (30 g.) was added in small quantities at a time, the whole being cooled in a freezing mixture. The clear solution was allowed to stand for about an hour and concentrated hydrochloric acid (44 c.c.) was gradually run in with constant shaking, the temperature being kept below −10°. After 24 hours, more hydrochloric acid was added, and the mixture left

for another day at the ordinary temperature; it was then warmed on the steam-bath for 10 minutes and extracted with ether. The ethereal solution was washed with a solution of sodium carbonate, dried, and evaporated. The residual oil, consisting of nearly pure cyano-lactone, was then hydrolysed with an excess of concentrated hydrochloric acid on the steam-bath. The clear solution was evaporated, and the solid extracted with chloroform or ethyl acetate; the residue which remained after the removal of the solvent crystallised from ethyl acetate and light petroleum (b. p. 60—80°) in long, colourless, flattened needles, m. p. 139—140°. The product was identified with the lactonic acid obtained in the bromination of α-methyl*cyclo*pentane-1 : 1-diacetic acid by direct comparison and by analysis (Found: C, 60·8; H, 7·3. Calc.: C, 60·6; H, 7·1%).

D. *Synthesis of α-Methyl*cyclo*pentylideneacetone* (XXVIII) *and of α-Methyl-Δ^1-*cyclo*pentenylacetone* (XXX).

*α-Methyl*cyclo*pentylideneacetic Acid* (XXVII).—The condensation of *cyclo*pentanone with ethyl α-bromopropionate and magnesium proceeded readily in benzene solution, giving a 50% yield of ethyl 1-hydroxy-α-methyl*cyclo*pentane-1-acetate, b. p. 130—140°/36 mm. The ester on hydrolysis with 50% alcoholic potash at the ordinary temperature yielded the hydroxy-acid as a viscous oil which showed no tendency to solidify; it was therefore boiled with acetic anhydride, and the mixture distilled in steam; the unsaturated acid, which separated from the distillate as a solid, crystallised from dilute methyl alcohol in needles, m. p. 108—109° (Found, for silver salt: Ag, 43·8. Calc.: Ag, 43·7%). The *acid chloride*, prepared in the usual way with thionyl chloride, distilled as a colourless liquid, b. p. 123°/30 mm.

*α-Methyl*cyclo*pentylideneacetone.*—This ketone was prepared in a good yield by the action of zinc methyl iodide on the foregoing acid chloride. With semicarbazide acetate it readily yielded a *semicarbazone*, of which two different forms were isolated by repeated crystallisation from methyl alcohol. The less soluble separated in rosettes of small crystals, m. p. 189° (Found: C, 61·6; H, 8·8; N, 21·7. $C_{10}H_{17}O_3N$ requires C, 61·5; H, 8·7; N, 21·5%), and the *ketone*, regenerated from it in the usual way, was obtained as a colourless oil, b. p. 108°/27 mm., $d_{4^\circ}^{19\cdot2^\circ}$ 0·960808, $n_D^{19\cdot2^\circ}$ 1·49642, $[R_L]_D$ 41·986 (calc., 41·106) (Found: C, 78·0; H, 10·2. $C_9H_{14}O$ requires C, 78·3; H, 10·1%). The more soluble semicarbazone crystallised from dilute alcohol in colourless, felted needles, m. p. 169° (Found: C, 61·8; H, 8·8; N, 21·6%), and the ketone regenerated from it had b. p. 109°/25 mm., $d_{4^\circ}^{20\cdot3^\circ}$ 0·958084, $n_D^{20\cdot3^\circ}$ 1·49528, $[R_L]_D$ 42·025 (Found: C, 77·9; H, 9·9%). The physical properties of the ketones corresponded well with their αβ-structure.

α-Methyl-Δ¹-cyclopentenylacetic Acid.—The ethyl ester was readily obtained by the dehydration of the hydroxy-ester (above) with the theoretical amount of phosphorus oxychloride in benzene solution: it distilled as a colourless oil with an agreeable smell, b. p. 108—110°/30 mm., $d_4^{17°}$ 0·96668, $n_D^{17°}$ 1·4583, $[R_L]_D$ 47·45 (calc., 47·37). The acid, prepared from this ester by hydrolysis with alcoholic potash, distilled as a colourless oil, b. p. 150°/28 mm., $d_4^{19.7°}$ 1·050988, $n_D^{18.7°}$ 1·4792, $[R_L]_D$ 37·79 (calc., 38·01) (Found, for Ag salt: Ag, 44·0. Calc.: Ag, 43·7%). A sample did not deposit any crystals during 14 months (compare Wallach, *loc. cit.*). The *acid chloride*, prepared in the usual way, had b. p. 86—88°/20 mm., and on treatment with zinc methyl iodide gave a good yield of the corresponding βγ-ketone. The crude ketone readily yielded a *semicarbazone*, which separated in lustrous plates, m. p. 144°, from dilute alcohol (Found: C, 61·8; H, 8·7; N, 21·8. $C_{10}H_{17}O_3N$ requires C, 61·5; H, 8·7; N, 21·5%), and *α-methyl-Δ¹-cyclopentenylacetone*, regenerated from it by means of oxalic acid, had b. p. 82°/17 mm., $d_4^{20°}$ 0·921922, $n_D^{20°}$ 1·4632, $[R_L]_D$ 41·24 (calc., 41·11) (Found: C, 78·7; H, 10·3. $C_9H_{14}O$ requires C, 78·3; H, 10·1%). The ketones could not be induced to react with ethyl sodiomalonate or sodiocyanoacetate.

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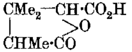
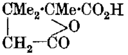
CCXLIV.—*Experiments on the Synthesis of Certain γ-Ketonic Acids Closely Allied to Balbiano's Acid. Part II. Syntheses of αββ- and ααβ-Trimethyllævulic Acids, of the Lactone of α′-Hydroxy-ααβ-trimethylglutaric Acid, and of γ-Keto-αββ-trimethylpropane-αγ-dicarboxylic Acid (Balbiano's Acid).*

By JOGENDRA CHANDRA BARDHAN.

DURING his classical experiments on the oxidation of camphoric acid (*e.g.*, *Rend. Accad. Lincei*, 1892, i, 278; *Ber.*, 1894, **27**, 2133), Balbiano isolated a considerable quantity of a dibasic acid, $C_8H_{12}O_5$,

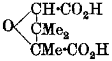
and an equivalent of oxalic acid, along with small amounts of camphanic, camphoronic, and trimethylsuccinic acids. The new acid, on reduction with hydriodic acid and red phosphorus, yielded a mixture of a monobasic lactonic acid, $C_8H_{12}O_4$, and a dibasic acid, $C_8H_{14}O_4$, which Balbiano considered to be αββ-trimethylglutaric acid because on oxidation it gave *as*-dimethylsuccinic acid. This structure was subsequently confirmed when Perkin and Thorpe synthesised the acid (J., 1899, **75**, 61).

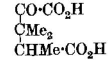
Since the trimethylglutaric acid is also formed from the lactonic acid $C_8H_{12}O_4$ on reduction, the latter might have been either (I) or (II), but Blanc (*Bull. Soc. chim.*, 1901, **25**, 68) synthesised the acid (II) and found it to be different from Balbiano's lactonic acid, which is therefore (I) (compare Pandya and Thorpe, J., 1923, **123**, 2852).

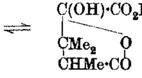
(I.)   (II.)

For many years two views were held as to the constitution of the acid $C_8H_{12}O_5$: Balbiano (*Ber.*, 1897, **30**, 289, 1901), as a result of his examination of the reduction products, represented the acid by the oxide formula (III), and suggested that the corresponding dihydroxy-acid was a stage in its formation from camphoric acid; whereas Mahla and Tiemann (*Ber.*, 1895, **28**, 2151) preferred the keto-formula (IV) on account of the fact that the acid, when heated at 160—180°, is completely decomposed with the formation of trimethylsuccinic anhydride and carbon monoxide. These authors could not, however, satisfactorily establish the ketonic character of the acid, and the somewhat ill-defined *p*-bromophenylhydrazone which they prepared proved to be an addition product (compare Balbiano, *loc. cit.*).

More recently, Kon, Stevenson, and Thorpe (J., 1922, **121**, 656) were led to represent the acid in the liquid state or in solution as an equilibrium mixture of the forms (IV) and (V), and this tautomeric structure was further supported by Rothstein, Stevenson, and Thorpe (J., 1925, **127**, 1078). Although it had thus been shown that


(III.)


(IV.)

 (V.)

Balbiano's oxide structure is incorrect, it was still necessary to prove definitely the correctness of the keto-formula, and this has now been achieved by the synthesis of an acid of this structure which is identical with the acid obtained from camphoric acid.

αββ-Trisubstituted ketoglutaric acids are peculiarly difficult to prepare, for the usual methods of synthesis fail, but since it had been

found (preceding paper) that ethyl 1-acetyl*cyclo*pentane-1-acetate treatment with alkaline permanganate was smoothly oxidised α-keto*cyclo*pentane-1 : 1-diacetic acid, it appeared possible that t desired ketonic acid might be obtainable by similarly oxidising t acetyl group of αββ-trimethyl-lævulic acid to the $CO{\cdot}CO_2H$ grou

Synthesis of αββ-Trimethyl-lævulic Acid.—This acid was prepa by the following series of reactions: Trimethylsuccinic anhydri was converted by sodium ethoxide into the half ester (VI), the a chloride of which reacted with zinc methyl iodide to give the ke ester (VII) in good yield. This ester, however, contained

(VI.)	(VII.)	(VIII.)
$CMe_2{\cdot}CO_2H$ / $CHMe{\cdot}CO_2Et$	$CMe_2{\cdot}CO{\cdot}CH_3$ / $CHMe{\cdot}CO_2Et$	$CMe_2{\cdot}CO_2Et$ / $CHMe{\cdot}CO{\cdot}CH_3$

appreciable quantity of the isomeric ester (VIII), evidently deri from the alternative acid ester formed during esterification of t anhydride. A somewhat similar mixture of ketonic esters was a obtained when the acid ester was prepared by the partial saponif ation of the neutral ester. Bone, Sudborough, and Spranklin statement (J., 1904, **85**, 536), that they obtained two different ac esters of trimethylsuccinic acid according as they started from t anhydride or the neutral ester, must therefore be regarded incorrect.

The separation of the pure constituents from the mixture of t corresponding acids thus obtained proved to be very difficult, b was ultimately accomplished by the fractional crystallisation of t mixed semicarbazones from methyl alcohol. The regenerated aci melted at 65—66° and 77—78°, and since they showed mutu depression of m. p. when mixed, there can be no doubt that they a different. Their respective structures were therefore ascertain by effecting a rational synthesis of ααβ-trimethyl-lævulic aci which proved to be identical with the less fusible acid, so the ac of m. p. 65—66° must be the αββ-isomeride.

Synthesis of ααβ-Trimethyl-lævulic Acid.—The first experiment t be tried for this purpose was the reaction of ethyl α-bromo*iso*butyra with ethyl sodiomethylacetoacetate, since it was expected that t condensation product would give the required acid (IX) on hydrolysi

$$\begin{matrix} CMe_2\text{—}CMe{\cdot}CO{\cdot}CH_3 \\ CO_2Et \quad CO_2Et \end{matrix} \longrightarrow \begin{matrix} CMe_2{\cdot}CHMe{\cdot}CO{\cdot}CH_3 \\ CO_2H \end{matrix} \quad \text{(IX.)}$$

but the condensation did not proceed in the expected manner, an all efforts to obtain this acid from the products of the reaction we fruitless.

It was then thought possible that methylmesityl oxide mig react with hydrocyanic acid according to the method of Lapwor

(J., 1904, **85**, 1216) to give a product which on hydrolysis should furnish the desired keto-acid :

$$CMe_2{:}CMe{\cdot}CO{\cdot}CH_3 \longrightarrow CMe_2(CN){\cdot}CHMe{\cdot}CO{\cdot}CH_3 \longrightarrow \text{(IX.)}$$

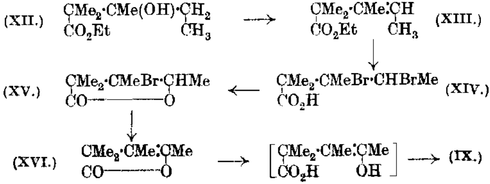
Although methylmesityl oxide was readily synthesised from trimethylacrylic acid (Blaise reaction), it reacted with hydrocyanic acid with such reluctance under the usual conditions that after prolonged heating there was obtained a considerable quantity of a stable cyanohydrin (X), evidently produced by the further action of hydrocyanic acid on the mononitrile first formed; traces of the expected acid (IX) were isolated in the form of its semicarbazone, but in insufficient quantity for characterisation.

The cyanohydrin (X) on hydrolysis yielded a nitrogenous *substance* (XI), closely analogous to mesitylic acid prepared by Pinner (*Ber.*, 1881, **14**, 1075) and by Lapworth (*loc. cit.*) from mesityl oxide by a somewhat similar process.

$$CMe_2(CN){\cdot}CHMe{\cdot}CMe(OH){\cdot}CN \quad \text{(X.)}$$

$$\underset{CO\text{———————}NH}{CMe_2{\cdot}CHMe{\cdot}CMe{\cdot}CO_2H} \quad \text{(XI.)}$$

Ultimately the following method was devised and found to give the desired synthesis. Methyl ethyl ketone was condensed with ethyl α-bromo*iso*butyrate and zinc, a good yield of *ethyl* β-*hydroxy*-ααβ-*trimethyl*-n-*valerate* (XII) being obtained. This hydroxy-ester on dehydration with phosphorus pentoxide yielded *ethyl* ααβ-*trimethyl*-Δ^{β}-*pentenoate* (XIII), the structure of which was established by oxidation with ozone, one of the products being acetaldehyde. When the corresponding *acid* was treated with bromine, it gave a somewhat unstable dibromide (XIV), which at the moment of its formation partly eliminated hydrobromic acid with the production of the bromo-lactone (XV) (compare Perkin and Smith, J., 1904, **85**, 157); but on distillation of the crude bromination product under the ordinary pressure, a considerable evolution of hydrobromic acid took place, and the chief product was the unsaturated *lactone* (XVI). This was finally hydrolysed by means of alcoholic potash to *ααβ-trimethyl-lævulic acid* (IX), presumably through the intermediate stage shown.



In spite of the many stages involved in the above synthesis, th yield of the keto-acid was quite good. The synthetic acid agreed i all its properties with the acid, m. p. 77—78°, prepared from tri methylsuccinic anhydride (above).

Synthesis of Balbiano's Acid.—αββ-Trimethyl-lævulic acid wa readily oxidised by alkaline permanganate to γ-keto-αββ-trimethyl propane-αγ-dicarboxylic acid. The acid thus obtained melted a the same temperature as Balbiano's acid, and showed no depressio of m. p. when mixed with an equal quantity of the acid obtained from camphoric acid (kindly lent by Professor Thorpe). The identity of the synthetic acid was also established by the pre- paration of its quinoxaline derivative, and by its conversion into αββ-trimethylglutaric acid by means of hydriodic acid and red phosphorus. Finally, the synthetic acid when heated is converted into trimethylsuccinic acid with evolution of carbon monoxide.

The synthesis of Balbiano's acid just described is consistent only with the keto-formula, and the solid acid most probably exists in this form; this follows, not only because Balbiano's acid does not give ψ-esters corresponding to the lactol form (compare for instance, opianic acid, phthalonic acid, and the semi-aldehyde of trimethyl-succinic acid), but also because on treatment with acetic anhydride it forms a normal anhydride (Balbiano, *Ber.*, 1897, **30**, 1902) and not an acetyl derivative.

In the light of the keto-formula, the anhydride of the acid should be represented by (XVII) (compare 3 : 4-dimethoxyphthalonic anhydride; Kuroda and Perkin, J., 1923, **123**, 2094). The anhydride reacts normally with β-naphthylamine, giving a crystalline naphthylamic acid (XVIII), which does not react with *o*-phenylene-diamine.

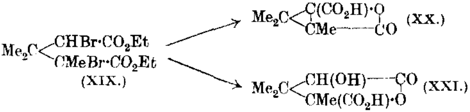
$$\text{(XVII.)}\ \begin{array}{l}\text{CMe}_2\text{–CO–CO}\\ \text{CHMe·CO·O}\end{array} \longrightarrow \begin{array}{l}\text{CMe}_2\text{·CO·CO·NH·C}_{10}\text{H}_7\\ \text{CHMe·CO}_2\text{H}\end{array}\ \text{(XVIII.)}$$

The formation of an acid of the keto-formula from camphoric acid is somewhat remarkable. Kon, Stevenson, and Thorpe (*loc. cit.*) suggested the following mechanism of its formation, starting from αα′-dihydroxy-αββ-trimethylglutaric acid, which, according to Balbiano, constitutes the first step in the oxidation of camphoric acid :

$$\text{Me}_2\text{C}\!<\!\begin{array}{l}\text{CH(OH)·CO}_2\text{H}\\ \text{CMe(OH)·CO}_2\text{H}\end{array} \rightarrow \text{Me}_2\text{C}\!<\!\begin{array}{l}\text{C(OH)·CO}_2\text{H}\\ \text{CMe·CO}_2\text{H}\end{array} \rightarrow \text{Me}_2\text{C}\!<\!\begin{array}{l}\text{CO·CO}_2\text{H}\\ \text{CHMe·CO}_2\text{H}\end{array}$$

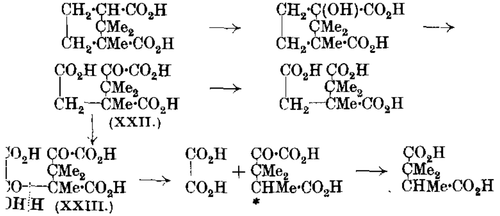
In spite of the apparent simplicity of this explanation, the issue is not in reality quite so clear, for it has been shown by Pandya and Thorpe (*loc. cit.*) that the dibromo-ester (XIX) on treatment with alkali passes into a mixture of the lactonic acids (XX) and (XXI),

from which no trace of any keto-acid can be obtained. Since the dihydroxytrimethylglutaric acids, which are presumably formed in these reactions, show no tendency whatever to pass into a hydroxy-*cyclo*propane acid, it follows that Balbiano's acid cannot be formed from camphoric acid by way of dihydroxytrimethylglutaric acid.



Quite apart from this, it is difficult to understand why camphoric acid, which is such an exceedingly stable substance, should undergo oxidative fission at those bonds which would have to be ruptured in order to give this dihydroxyglutaric acid—a mode of oxidation which suggested to Balbiano his oxide structure.

There is, however, no need to assume the formation of a dihydroxyglutaric acid. An adequate explanation is provided for the formation, not only of the keto-acid, but also of the accompanying camphanic, camphoronic, and trimethylsuccinic acids, if it be assumed that the oxidation of camphoric acid proceeds through the following stages :



A similar mechanism has been postulated by Bredt (*Ber.*, 1893, **26**, 3050) in order to explain the formation of camphoronic acid from camphoric acid by oxidation with nitric acid, but there is a difference between the two cases in that the intermediate keto-acid (XXII) is somewhat stable towards alkaline permanganate and is not therefore broken down into camphoronic acid to any large extent; on the contrary it is oxidised at the methylene group and the resulting diketo-acid (XXIII) is hydrolysed as shown above.

The formation of an α-ketonic acid by the direct oxidation of an acetic acid residue is not without precedent, for Chandrasena and

Ingold (J., 1922, **121**, 1553) have shown that α-campholenic aci on treatment with mild oxidising agents gives a keto-acid as th principal product :

Owing to the obvious difficulty of devising suitable experiments, has not been found possible definitely to establish the correctne of the mechanism suggested above. It is hoped, however, that th experiments on the oxidation of camphanic, dehydrocamphori and camphoronic acids, which are now in hand, will throw furth light on the matter.

The keto-acid contains an asymmetric carbon atom (marked and would therefore be expected to exist in one inactive and tw active modifications. The acid actually isolated by Balbian from *d*-camphoric acid was, however, inactive. This is to b expected, for examination of the scheme above shows that durin the hydrolysis of the diketo-acid (XXIII) a new asymmetric carbo atom is being produced, and consequently the resulting produc should be inactive owing to the formation in equal quantities o the two optically enantiomorphous forms. The case of camphoroni acid is somewhat different because it still retains one of th asymmetric carbon atoms originally present in the camphoric acid

Balbiano (*Ber.*, 1899, **32**, 1022) apparently succeeded in resolvin his acid, $C_8H_{12}O_5$, by a fractional crystallisation of its quinine salts but the rotations, $[\alpha]_D + 5{\cdot}48°$ and $- 3{\cdot}35°$, which he found for th two active forms are far from satisfactory. Experiments are now being undertaken to prepare the two active modifications of the aci from the *d*- and *l*-modifications of trimethylsuccinic acid by applyin the same scheme as has been used for the synthesis of the inactiv acid.

During the course of the foregoing experiments a considerabl quantity of ααβ-trimethyl-lævulic acid had accumulated, and i seemed of interest to investigate whether on oxidation with alkalin permanganate it would give the keto-acid

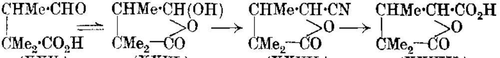
$$CO_2H{\cdot}CMe_2{\cdot}CHMe{\cdot}CO{\cdot}CO_2H \quad (XXIV.),$$

but it was found to yield only trimethylsuccinic acid. This i somewhat remarkable, especially as Baeyer, in the course of th oxidation of pinene, isolated an appreciable quantity of a keto-aci which he considered to be formed by the oxidation of pinonic acid

$$CO_2H{\cdot}CH_2{\cdot}CH{<}{}^{CH_2}_{CMe_2}{>}CH{\cdot}CO{\cdot}CH_3 \longrightarrow$$

$$CO_2H{\cdot}CH_2{\cdot}CH{<}{}^{CH_2}_{CMe_2}{>}CH{\cdot}CO{\cdot}CO_2H$$

Attempts were also made to prepare the keto-acid (XXIV) by the oxidation of the lactonic acid (XXVIII), which was obtained in good yield by the action of hydrocyanic acid on the lactone (XXVI) (Blaise and Courtout, *Bull. Soc. chim.*, 1902, **35**, 998), followed by the hydrolysis of the lactonic nitrile (XXVII) with the aid of concentrated hydrochloric acid, the reaction probably taking place through the tautomeric aldehyde-form (XXV). Theoretically, the



(XXV.) (XXVI.) (XXVII.) (XXVIII.)

lactonic acid should exist in two inactive forms, but only one has yet been isolated. On treatment with alkaline permanganate, the lactonic acid passes into trimethylsuccinic acid, no trace of the desired keto-acid being formed, although Balbiano's lactonic acid (I) under similar conditions furnishes the keto-acid (IV). Further experiments for the synthesis of the keto-acid are in progress.

EXPERIMENTAL.

Preparation of Trimethylsuccinic Acid.—At the commencement of this research most of the trimethylsuccinic acid was prepared according to the method of Bone and Sprankling (J., 1899, **75**, 862). It was subsequently found, however, that Higson and Thorpe's method (J., 1906, **89**, 1466) was by far the best for obtaining the acid in quantity.

The condensation of acetonecyanohydrin with ethyl sodiocyanoacetate is best carried out as follows: A suspension of the sodio-derivative of ethyl cyanoacetate, prepared from sodium (30 g.), alcohol (480 c.c.), and cyanoacetic ester (155 c.c.), was gradually added with vigorous shaking to a solution of freshly distilled acetonecyanohydrin (118 g.) in 80 c.c. of alcohol, cooled in ice. The product was kept in ice for 12 hours and then at the ordinary temperature for 2 days. The viscous mass was mixed with methyl iodide (90 c.c.) and gently heated under reflux until neutral; the ethyl αβ-dicyano-αββ-trimethylpropionate, b. p. 159—162°/25 mm., isolated in the usual way, was hydrolysed by 12 hours' boiling with seven times its volume of concentrated hydrochloric acid, thus giving an almost quantitative yield of trimethylsuccinic acid, which had m. p. 149° after one crystallisation from dilute hydrochloric acid.

The anhydride, prepared by boiling the acid with an excess of acetyl chloride, is best purified by distillation under reduced pressure from a Claisen flask provided with a fractionating side arm. It is obtained as a colourless oil, b. p. 110°/10 mm., which on cooling

solidifies to a crystalline mass (Found: C, 58·8; H, 7·3. Calc.: C, 59·2; H, 7·0%).

Synthesis of αββ-*Trimethyl-lævulic Acid* (formula as VII).—*Action of sodium ethoxide on trimethylsuccinic anhydride.* To the anhydride (35·5 g.), dissolved in absolute alcohol (120 c.c.) and cooled in a freezing mixture, was gradually added a solution of sodium ethoxide (sodium, 5·75 g.; alcohol, 144 c.c.) so that the temperature did not rise above 0°; after 2—3 hours the excess of alcohol was distilled off under reduced pressure at 40°. The solid residue was dissolved in water, and the solution extracted with ether to remove any neutral ester. The aqueous solution was slightly acidified with dilute sulphuric acid, and the liberated oil collected in ether. On drying and distilling off the ether, a viscous oil remained which did not solidify in a vacuum, and when cooled in a freezing mixture passed into a thick jelly-like mass (Found, in silver salt: Ag, 38·8. Calc.: Ag, 38·4%). It decomposed on distillation under reduced pressure (compare Bone, Sudborough, and Sprankling, *loc. cit.*, p. 551).

The acid ester (42 g.) was warmed with freshly distilled thionyl chloride (25 c.c.) in a glycerol-bath at 55°, and excess of thionyl chloride was removed under diminished pressure. The residual oil was dissolved in an equal volume of dry benzene, and the solution gradually added to a solution of zinc methyl iodide, prepared by heating over-night a mixture of zinc copper couple (60 g.), benzene (30 c.c.), methyl iodide (30 c.c.), and ethyl acetate (15 c.c.); the mixture was vigorously shaken and kept at 0° during the reaction, and then allowed to attain the ordinary temperature (1 hour). Dilute sulphuric acid was added, the benzene layer separated, washed successively with dilute caustic potash solution, water, and saturated ammonium sulphate solution, dried, and the solvent removed. The residue on distillation under diminished pressure boiled constantly at 113°/18 mm., giving a colourless oil with a terpene-like smell. Preliminary examination showed this to consist of a mixture of several substances, which were separated as follows: The oil (30 g.) was heated under reflux for 1 hour with a solution of potassium hydroxide (30 g.) in water (30 c.c.) and methyl alcohol (60 c.c.); the excess of alcohol was evaporated, the residue extracted with ether to remove unchanged ester, the aqueous solution acidified, again extracted with ether, and the solvent removed. The residual oil (24 g., moist) was dissolved in water (30 c.c.) and the solution gently warmed on the steam-bath for ½ hour with the addition of semicarbazide hydrochloride (15 g.), sodium acetate (30 g.), and water (60 c.c.). On standing at the ordinary temperature for 20 hours, a considerable amount of a crystalline semicarbazone separated; this

was collected and the filtrate extracted several times with ether, dried, and evaporated, giving an oil which, when purified in the usual way, proved to be trimethylsuccinic acid.

The crude semicarbazone was repeatedly crystallised (at least 20 times) from methyl alcohol, whereby two fractions were obtained, m. p.'s 174° and 155°, together with a large middle fraction melting indefinitely between 160—168°, from which no definite product could be isolated. The *semicarbazone*, m. p. 155°, is readily soluble in methyl alcohol and crystallises in minute, colourless prisms (Found: C, 50·1; H, 7·9. $C_9H_{17}O_3N_3$ requires C, 50·2; H, 7·9%).

The pure semicarbazone (17 g.) was heated on the steam-bath with concentrated hydrochloric acid (25 c.c.) and water (25 c.c.) until the crystals had entirely disappeared. The product was then extracted with ether and dried. The residue obtained on evaporation of the ether readily solidified in an evacuated desiccator to a crystalline mass (10 g.). (It is essential that the semicarbazone used be very pure; otherwise the acid is obtained as a gum which is difficult to purify.)

αββ-*Trimethyl-lævulic acid* crystallises from light petroleum (b. p. 40—60°) in clusters of flattened prisms, m. p. 65—66° (Found: C, 60·9; H, 8·9. $C_8H_{14}O_3$ requires C, 60·8; H, 8·9%), moderately soluble in most solvents. The *ethyl* ester, prepared from the pure acid by Phelp and Tillotson's alcohol-vapour method, had b. p. 110°/14 mm., $d_4^{19°}$ 0·981537, $n_D^{19°}$ 1·43638, $[R_L]_D$ 49·6 (calc., 50·0) (Found: C, 64·3; H, 9·8. $C_{10}H_{18}O_3$ requires C, 64·5; H, 9·7%).

The less soluble *semicarbazone* crystallises from methyl alcohol in beautiful iridescent prisms, m. p. 174° (Found: C, 50·2; H, 7·7. $C_9H_{17}O_3N_3$ requires C, 50·2; H, 7·9%). When this was treated with dilute hydrochloric acid, as described for the other semicarbazone, ααβ-*trimethyl-lævulic acid* was obtained as an oil which gradually solidified to a hard crystalline mass; it was purified by careful evaporation of its ice-cold solution in ethyl bromide–light petroleum (b. p. 40—60°), and thus obtained in minute, transparent prisms, m. p. 77—78° (mixed m. p. with αββ-trimethyl-lævulic acid, 52°) (Found: C, 60·8; H, 8·9. $C_8H_{14}O_3$ requires C, 60·8; H, 8·9%). Its constitution follows from its rational synthesis (see below).

Oxidation of αββ-*Trimethyl-lævulic Acid with Sodium Hypobromite.*—The pure acid (1 g.) was dissolved in aqueous caustic potash, cooled to 0°, and mixed with a solution of potassium hypobromite, prepared from bromine (1 c.c.), potassium hydroxide (2·5 g.), and water (45 c.c.). After remaining for 3 hours, the liquid was treated with sulphur dioxide, strongly acidified with dilute sulphuric acid, and extracted with ether. The dried extract on evaporation left a solid residue which was identified as trimethylsuccinic acid by its m. p. and by direct comparison.

Attempted Synthesis of ααβ-Trimethyl-lævulic Acid (IX).

Trimethylacrylic Acid.—Ethyl β-hydroxy-αββ-trimethylpropiona was prepared by the condensation of acetone with ethyl α-brom propionate and zinc in accordance with the directions of Perkin ar Thorpe (J., 1896, **69**, 1482), and obtained as a colourless oil, b. : 99°/28 mm. The low-boiling fractions on distillation at the ordinai pressure yielded an appreciable amount of mesityl oxide. Tl hydroxy-ester (32 g.) was gradually mixed with phosphorus pent chloride (50 g.), and the clear liquid gently heated on the steam-bat for 1 hour. After being cooled, the product was poured into ic water, the oil extracted with ether, and the solvent evaporated. Tl residue was hydrolysed by boiling with an excess of alcohol potash, and after removal of the excess of alcohol, the solution wa acidified, extracted with ether, the extract dried, and the eth evaporated. On distillation, αββ-trimethylacrylic acid was obtaine as a colourless oil, b. p. 114—115°/27 mm., which partly solidifie on cooling, and was recrystallised from methyl alcohol; colourles plates, m. p. 70—71° (Found: C, 63·1; H, 8·8. Calc.: C, 63·2 H, 8·8%).

Methylmesityl Oxide.—αββ-Trimethylacrylyl chloride, b. p. 144—145°/766 mm. (compare Perkin and Thorpe, *loc. cit.*, p. 1480), wa treated with zinc methyl iodide in the usual way and the keton isolated and distilled (b. p. 145°); its *semicarbazone* separated fron dilute alcohol in colourless plates, m. p. 186° (Found: C, 57·3 H, 8·9. $C_8H_{15}ON_3$ requires C, 56·8; H, 8·9%). Methylmesity oxide condensed with malonic ester under the following conditions A solution of ethyl sodiomalonate (sodium, 1·15 g.; absolut alcohol, 14 c.c.; ethyl malonate, 8·5 g.) was heated under reflu with methylmesityl oxide (5·6 g.) for 18 hours; the excess of alcoho was distilled off, the mixture diluted with water (100 c.c.), and th neutral products were extracted with ether. The aqueous solutio was then mixed with potassium hydroxide (4·5 g.), the whole boile for 15 minutes, acidified with dilute sulphuric acid, and boiled unti no more carbon dioxide was evolved; the yellow oil which separate solidified on cooling and was crystallised from water (charcoal) wit the addition of a few drops of alcohol. The colourless needles m. p. 100—101°, were evidently trimethyldihydroresorcinol (compar Crossley, J., 1901, **79**, 141) (Found: C, 70·1; H, 9·3. Calc.: C 70·1; H, 9·1%).

Action of Potassium Cyanide on Methylmesityl Oxide.—Attempt to condense the ketone with 1 mol. of hydrocyanic acid were fruitless for its reaction with 2 mols. could not be prevented. The ketone (11·2 g.) was dissolved in alcohol (75 c.c.), and the solution boiled under reflux with potassium cyanide (26 g. in 78 c.c. of water)

for 4 hours. The mixture was evaporated on the steam-bath, and the viscous product boiled with a large excess of concentrated hydrochloric acid. The excess of acid was then removed, and the solid residue mixed with water and filtered. The solid (XI) was crystallised (charcoal) from acetic acid, separating in colourless, silky needles, m. p. 238° (decomp.) (Found : C, 58·4; H, 8·1. $C_9H_{15}O_3N$ requires C, 58·4; H, 8·1%), easily soluble in glacial acetic acid, moderately soluble in boiling acetone, and sparingly soluble in other organic solvents. The compound was acidic, and resembled mesitylic acid in its general properties.

The aqueous filtrate (above) was repeatedly extracted with ether, and the extract dried and evaporated; the oily residue readily gave a crystalline semicarbazone, which separated from alcohol in colourless, shining prisms, m. p. 175° (decomp.) (Found : C, 50·5; H, 8·1. $C_9H_{17}O_3N_3$ requires C, 50·2; H, 7·9%). There can be no doubt that this is the semicarbazone of ααβ-trimethyl-lævulic acid, but owing to the small yield the solid acid could not be obtained from it.

Synthesis of ααβ-Trimethyl-lævulic Acid.

*Ethyl β-Hydroxy-ααβ-trimethyl-*n*-valerate* (XII).—A mixture of dry methyl ethyl ketone (55 g.), ethyl α-bromo*iso*butyrate (150 g.), benzene (300 c.c.), and zinc turnings (60 g.) was boiled under reflux on the steam-bath for ½ hour. Minute quantities of iodine were then added until the reaction started. The flask was removed from the steam-bath and the vigorous reaction allowed to proceed by its own heat, the mixture being finally heated on the steam-bath for 15 minutes. *Ethyl β-hydroxy-ααβ-trimethyl-*n*-valerate* was isolated from the mixture and purified in the usual way, being obtained as a colourless, mobile oil, having a faint ethereal smell (yield, 55%), b. p. 92°/11 mm. (Found : C, 63·5; H, 10·2. $C_{10}H_{20}O_3$ requires C, 63·8; H, 10·6%).

ααβ-Trimethyl-Δ^{β}-pentenoic Acid (formula as XIII).—The hydroxy-ester (68 g.) was mixed with phosphorus pentoxide (40 g.) under dry benzene (75 c.c.), and the mixture was slowly distilled under ordinary pressure until most of the benzene had passed over. The distillation was then continued under reduced pressure and a considerable amount of a low-boiling fraction collected; on redistillation, almost the whole fraction boiled at 100—102°/45 mm., giving the *ester* (XIII) as a colourless, transparent oil, having a sweet smell; $d_4^{16\cdot8°}$ 0·906942, $n_D^{16\cdot8°}$ 1·43878, $[R_L]_D$ 49·3 (calc., 49·5) (Found : C, 70·1; H, 10·8. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·6%). A chloroform solution of the ester was ozonised and then gave a good yield of acetaldehyde, identified as ethylidene-β-dinaphthyl oxide, m. p. 170° (mixed m. p. with an authentic specimen 171°).

The ester was hydrolysed with 10% methyl-alcoholic potash, and the resulting *αaβ-trimethyl-Δ^β-pentenoic acid* had b. p. 113°/10 mm., $d_4^{19\cdot2°}$ 0·963434, $n_D^{19\cdot2°}$ 1·45283, $[R_L]_D$ 39·8 (calc., 40·2) (Found, for *silver* salt: Ag, 43·8. $C_8H_{13}O_2Ag$ requires Ag, 43·4%); the p-*toluidide*, prepared from the acid chloride and *p*-toluidine, crystallised from light petroleum (b. p. 40—60°) in long, silky needles, m. p. 71° (Found: C, 77·9; H, 9·0. $C_{15}H_{21}ON$ requires C, 77·9; H, 9·1%).

Lactone of γ-Hydroxy-ααβ-trimethyl-Δ^β-pentenoic Acid (XVI).—The foregoing acid was dissolved in dry carbon disulphide, and to the solution, cooled to 0°, a slight excess of bromine was added. After remaining in the cold for a few hours, the solvent was removed. The solid residue thus obtained could not be purified owing to the ease with which it lost hydrobromic acid. The crude product was therefore distilled from a glycerol-bath; a considerable evolution of hydrobromic acid took place, and between 210° and 260° (bath temperature) a large amount of brown oil distilled over. This was collected in ether, washed with a dilute solution of sodium carbonate, dried with sodium sulphate, evaporated, and the residue distilled under reduced pressure. After several distillations, a considerable amount of a low-boiling fraction (b. p. 75—80°/13 mm.) was isolated, together with a small amount of a higher-boiling fraction (b. p. 110°/13 mm.) which still contained some bromine and was not further investigated. The first fraction was again washed with sodium carbonate, dried, and distilled, the *lactone* being obtained as a colourless, halogen-free liquid, b. p. 80°/13 mm., having a characteristic burning smell (Found: C, 68·7; H, 8·8. $C_8H_{12}O_2$ requires C, 68·6; H, 8·6%).

ααβ-Trimethyl-lævulic Acid (IX).—The unsaturated lactone was boiled under reflux with 20% methyl-alcoholic potash for 2 hours. The alcohol was evaporated, the residue acidified, and extracted six times with ether; when freed from solvent, ultimately in a vacuum desiccator over sulphuric acid, the acid was obtained as a colourless solid, m. p. 77—78° after recrystallisation from ethyl bromide–light petroleum (b. p. 60—80°) (Found: C, 60·7; H, 9·0. Calc. for $C_8H_{14}O_3$: C, 60·8; H, 8·9%), and was identical in all essential respects with the acid obtained previously (p. 2613), giving a semicarbazone, m. p. 173° (Found: C, 50·6; H, 7·9. Calc.: C, 50·2; H, 7·9%).

The p-*nitrophenylhydrazone* forms yellow, flattened needles, m. p. 207° (with previous softening), showing slight dichroism (Found: C, 57·2; H, 6·5. $C_{14}H_{19}O_4N_3$ requires C, 57·3; H, 6·5%). The *piperonylidene* derivative crystallises from dilute alcohol (charcoal) in lemon-yellow needles, m. p. 115° (Found: C, 66·2; H, 6·1. $C_{16}H_{18}O_5$ requires C, 66·2; H, 6·2%).

Synthesis and Properties of γ-Keto-αββ-trimethylpropane-αγ-dicarboxylic Acid (Balbiano's Acid) (IV).

Oxidation of αββ-Trimethyl-lævulic Acid.—To a mixture of αββ-trimethyl-lævulic acid (5 g.), potassium hydroxide (2 g.), and water (200 c.c.), was added a solution of permanganate (12 g.) and caustic potash (4 g.) in 300 c.c. of water, the mixture being cooled in running water. In the course of 2—3 hours the colour of the permanganate disappeared, and after a further 12 hours the greenish liquid became practically colourless. The manganese precipitate was collected and washed several times with hot water, and the combined aqueous filtrates were concentrated, cooled, acidified with hydrochloric acid, and extracted with ether. The solid residue (3·5 g.), which remained after removal of the last traces of ether in a vacuum desiccator, was exactly neutralised with caustic soda, mixed with a 30% solution of calcium chloride, filtered, and the clear solution boiled on a sand-bath for 1 hour. The crystalline precipitate which separated on cooling was collected, washed, suspended in water, and decomposed with concentrated hydrochloric acid in presence of an excess of ether. The ethereal layer was separated, washed, dried with anhydrous sodium sulphate, and evaporated. On being kept in a desiccator, the residue solidified to a snow-white, crystalline mass, which melted at 119° after having been rubbed with a little chloroform, and consisted of pure Balbiano's acid (Found: C, 51·1; H, 6·5. Calc.: C, 51·0; H, 6·4%). The identity was further established by direct comparison with an authentic specimen of the acid prepared from camphoric acid and by the following characteristic reactions.

(1) *Formation of quinoxaline derivative.* A considerable quantity of this substance accumulated in the course of the preliminary experiments on the oxidation of trimethyl-lævulic acid and its ethyl ester.* The crude acid resulting from the oxidation was mixed with an excess of *o*-phenylenediamine and glacial acetic acid and gently warmed on the steam-bath for ½ hour; excess of acetic acid was removed, and addition of a large excess of water then precipitated a solid which crystallised from methyl alcohol (charcoal) in magnificent shining plates, m. p. 223—224° with previous softening (mixed m. p. with an authentic specimen 223—224°; compare Kon, Stevenson, and Thorpe, *loc. cit.*) (Found: C, 64·5; H, 6·5. Calc.: C, 64·6; H, 6·2%).

* Owing to the extraordinary ease with which ethyl αββ-trimethyl-lævulate is hydrolysed by alkali, twice the theoretical quantity of permanganate must be used when this ester is employed in the synthesis of Balbiano's acid, as otherwise the alcohol produced reduces the whole of the permanganate, leaving the lævulic acid practically unchanged.

(2) *Formation of* αββ-*trimethylglutaric acid.* The synthetic acid (2 g.) was heated with hydriodic acid (12 c.c., *d* 1·9) and red phosphorus (1 g.) for 15 hours in a closed tube at 150—160°. The colourless solution was extracted with ether and the solid residue from the extract was dissolved in ammonia and boiled with a solution of calcium chloride. The precipitated calcium salt was collected and decomposed with dilute hydrochloric acid; the free acid, isolated in the usual way, crystallised from dilute hydrochloric acid in glistening prisms, m. p. 86—87° (Found: C, 55·4; H, 8·2. Calc.: C, 55·2; H, 8·1%).

(3) *Formation of trimethylsuccinic acid.* The crude oxidation acid was heated in a sulphuric acid bath, the melt extracted with boiling water, and the succinic acid isolated and purified in the form of its calcium salt; after one crystallisation from dilute hydrochloric acid it melted at 148° (compare Mahla and Tiemann, *loc. cit.*) (Found: C, 52·4; H, 7·5. Calc.: C, 52·5; H, 7·5%).

The following experiments were made with a specimen of Balbiano's acid prepared from camphoric acid by oxidation with alkaline permanganate (Balbiano, *loc. cit.*; Rothstein, Stevenson, and Thorpe, *loc. cit.*). The yield of the keto-acid is considerably reduced if the temperature is allowed to rise above 30°. The acid was isolated as the characteristic calcium salt and purified in the usual way.

The anhydride (XVII) was prepared by the following modification of Balbiano's method: The acid (5 g.) was boiled under reflux with acetic anhydride (20 c.c.) for 2 hours, the excess of acetic anhydride was removed under reduced pressure, and the residue kept in a desiccator. Since the product did not show any tendency to solidify, its constitution was confirmed by conversion into a crystalline naphthylamic acid by dissolving it in benzene and boiling the solution under reflux with a slight excess of β-naphthylamine for ½ hour. It was then diluted with ether and washed with dilute hydrochloric acid and water. The naphthylamic acid (XVIII) was dissolved in sodium carbonate and precipitated with dilute acid; it crystallised from dilute methyl alcohol (charcoal) in colourless, shining scales, m. p. 177° (decomp.), and behaved on titration as a monobasic acid (Found: C, 68·8; H, 6·3; *M*, 315. Calc.: C, 69·0; H, 6·1%; *M*, 313). It does not condense with *o*-phenylenediamine, and decomposes on heating with the formation of resinous products.

Action of Alkali on Balbiano's Acid.—The acid (5 g.) was boiled with a solution of potassium hydroxide (60 g.) in water (40 c.c.) for 3 hours, the product cooled in ice, acidified with hydrochloric acid, and extracted several times with ether. On evaporation of the solvent, a solid (3·9 g.) remained, which was proved to be unchanged

Balbiano's acid by its m. p. (119°) and by the formation of the quinoxaline derivative (m. p. 223—224°). Under the above conditions, therefore, Balbiano's acid remains practically unchanged and does not show any tendency to pass into a hydroxy*cyclo*propane acid.

Reduction with Sodium Amalgam.—The acid (5 g.) was dissolved in sodium carbonate and mechanically stirred with 300 g. of 3% sodium amalgam; the solution was concentrated, cooled, acidified with dilute hydrochloric acid, and extracted with ether. The residue from the ethereal extract was neutralised with alkali and boiled with a solution of calcium chloride to remove any unchanged keto-acid. The clear filtrate was acidified with hydrochloric acid and extracted with ether. The residue from evaporation of the extract was repeatedly crystallised from ethyl acetate–light petroleum (b. p. 60—80°) and yielded the expected lactonic acid in flattened needles, m. p. 163° (Found: C, 56·0; H, 7·3. Calc.: C, 55·8; H, 7·0%).

Attempt to Prepare the Keto-acid (XXIV).—The oxidation of ααβ-trimethyl-lævulic acid (IX) was carried out in an exactly similar manner to that of αββ-trimethyl-lævulic acid and appeared to proceed as before, but the product did not condense with *o*-phenylenediamine, and after recrystallisation from dilute hydrochloric acid it was identified as trimethylsuccinic acid, m. p. 149°.

Condensation of Chloroacetic Ester with Dimethylacetoacetic Ester.—Since a considerable amount of dimethylacetoacetic ester had accumulated in course of the preparation of ααβ-trimethylglutaconic acid, which had been used in unsuccessful efforts to prepare the lactone (XXVIII) by reduction, an attempt was made to convert it into the semi-aldehyde of trimethylsuccinic acid (XXV) by condensation with chloroacetic ester and sodium ethoxide (Darzens, *Compt. rend.*, 1904, **139**, 1215), followed by hydrolysis and distillation of the resulting oxidic ester, $CO_2Et\cdot CMe_2\cdot CMe\cdot CH\cdot CO_2Et$ (with an O bridge linking CMe and CH).

A mixture of dimethylacetoacetic ester (80 g.) and chloroacetic ester (90 g.) was cooled in a freezing mixture, and finely powdered sodium ethoxide (50 g.) added in small quantities with vigorous shaking. After remaining at the ordinary temperature over-night, the mixture was heated on the steam-bath for 5 hours. The dark-coloured mass was then mixed with water and extracted with ether. The ethereal extract was washed with sodium carbonate, dried, and evaporated. On distillation the residue gave a considerable amount of unchanged dimethylacetoacetic ester in the low-boiling fractions, and subsequently the oxidic *ester* was obtained as a colourless liquid, b. p. 162°/26 mm. (yield, 30%) (Found: C, 58·6; H, 7·8. $C_{12}H_{20}O_5$ requires C, 59·0; H, 8·2%). This ester on hydrolysis and

distillation yielded an extremely viscous oil, which did not give any semicarbazone and is still under investigation.

Synthesis of the Lactonic Acid (XXVIII).—Preliminary attempts were made to prepare this acid from ααβ-trimethylglutaric acid, but the latter could not be obtained in suitable condition either by Perkin and Thorpe's method (J., 1896, **69**, 1187), by catalytic reduction of the corresponding glutaconic acid, or by the condensation of *iso*butaldehyde with ethyl ethylidenemalonate. Ultimately, however, the semi-aldehyde of trimethylsuccinic acid was prepared by Blaise and Courtout's method (*loc. cit.*), and, although it exists in the lactol form (XXVI), it was found to condense with hydrocyanic acid, thereby enabling the synthesis to be effected as follows: A mixture of the semi-aldehyde (5 g.), potassium cyanide (98%, 9·2 g.), and water (15 c.c.) was cooled in a freezing mixture, and to it was gradually added (2 hours) the calculated amount of concentrated hydrochloric acid (11·5 c.c.); after remaining in the cold over-night, the mixture was warmed on the steam-bath with the addition of hydrochloric acid (5 c.c.). The resulting oil was collected in ether, washed with dilute sodium carbonate, dried, and the ether distilled off. The residue of almost pure *cyano-lactone* (XXVII) was hydrolysed with concentrated hydrochloric acid, and the clear solution extracted several times with ether. Removal of the solvent left an oil which slowly solidified to a crystalline mass, and repeated crystallisation from toluene gave the *lactone* of *α′-hydroxy-ααβ-trimethylglutaric acid* in stellate clusters of fan-shaped needles, m. p. 110° (Found: C, 55·5; H, 7·0. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%). The mother-liquor from the crystallisation yielded on evaporation a gum which was not further investigated. On oxidation with alkaline permanganate the lactonic acid gave trimethylsuccinic acid as the sole product.

αα-Dihydroxy-ββ-dimethylglutaric Acid.—This substance was prepared by the oxidation of ββ-dimethyl-lævulic acid with alkaline permanganate. The crude product, which was obtained as a gum, was dissolved in ammonia, and the sparingly soluble calcium salt precipitated by warming with a solution of calcium chloride. The acid was regenerated with dilute hydrochloric acid and extracted with ether. The solid residue, purified by repeated crystallisation from chloroform, was obtained in silky needles, m. p. 82–83° (Found: C, 43·9; H, 6·4. Calc.: C, 43·7; H, 6·3%); the identity of this substance with αα-dihydroxy-ββ-dimethylglutaric acid (Perkin and Thorpe, *J.*, *1901*, **79**, 757) was established by direct comparison and by a mixed m. p. This shows, therefore, that the method by which Balbiano's acid has been synthesised is a very general one.

I take this opportunity of expressing my indebtedness to Professor J. F. Thorpe, F.R.S., for his kind interest in the work and for the encouragement I have received from him. I am also indebted to the Trustees of the Palit Fund of the Calcutta University for a Foreign Scholarship, and to the Chemical Society for a grant for which grateful acknowledgments are made.

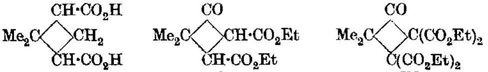
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, July* 11*th*, 1928.]

CCCXLV.—*Attempts to Synthesise Norpinic Acid.*

By GEORGE ROGER CLEMO and KENNETH NORMAN WELCH.

SINCE norpinic acid, one of the key compounds of terpene chemistry, was given the constitution (I) by Baeyer (*Ber.*, 1896, **29**, 1907), numerous unsuccessful attempts at its synthesis have been made. The claim of Ganguly (*J. Indian Inst. Sci.*, 1922, 23) must be included in this category, since, although it has only been possible to refer to an abstract of the paper, this states definitely that Ganguly's experiment cannot be regarded as successful. The following is a brief account of synthetic work designed to achieve this end, in which results of interest have been obtained although final success has not been reached. The continued inability to synthesise this acid is not easy to understand from Ingold's modification of the Baeyer strain theory (J., 1915, **107**, 197, 1082), in view of the fact that *cyclo*butane-1 : 3-dicarboxylic acid is easily prepared (Perkin and Simonsen, J., 1909, **95**, 1171).

The first synthetic method to be tried was to prepare (II) by condensing dimethylketen with maleic or fumaric ester. On hydrolysis, this should lose carbon dioxide, and the cyanohydrin of the resulting keto-acid by treatment with hydrobromic acid followed by the replacement of the bromine atom by hydrogen should yield (I).



(I.) (II.) (III.)

Only polymerised dimethylketen and unchanged ester, however, could be isolated from the reaction mixture, even when one or both of the reagents were produced *in situ*, and therefore presumably in an active phase, as by the action of a mixture of zinc and copper powder on an ethereal solution of α-bromo*iso*butyryl bromide and αβ-dibromosuccinic ester. Likewise, condensation could not be

effected between α-bromo*iso*butyryl bromide and sodioethanetetracarboxylic ester to give the compound (III).

The preparation of ethyl αα-dimethyltricarballylate,

$$CMe_2(CO_2Et)\cdot CH(CO_2Et)\cdot CH_2\cdot CO_2Et,$$

was then investigated with a view to carrying out the Dieckmann reaction on it to give (II). The corresponding acid has been obtained by the oxidation of pinic acid (Tiemann and Semmler, *Ber.*, 1895, **28**, 1349), of dihydroxycamphoceanic acid (Jagelki, *Ber.*, 1899, **32**, 1509), and of fenchone (Gardner and Cockburn, J., 1898, **73**, 708), and also synthetically from ethyl α-bromo*iso*butyrate and ethyl sodiocyanosuccinate, followed by hydrolysis. It was thought, however, that it might be easily prepared from the more accessible bromoacetic ester and sodio-αβ-dicyano*iso*valeric ester, which is readily obtained by the action of acetonecyanohydrin on sodium cyanoacetic ester (Higson and Thorpe, J., 1906, **89**, 1455). In spite of the fact, however, that a much improved method for the preparation of acetonecyanohydrin has been worked out, the poor yields of dimethyltricarballylic acid thus obtained render it impracticable to prepare thus the necessary amount for the full investigation of this synthetic method.

Attention was then directed to the action of formaldehyde and its derivatives on *iso*propylidenedimalonic ester, $CMe_2{:}[CH(CO_2Et)_2]_2$, which has been prepared from *iso*propylidenemalonic ester (Kötz, *J. pr. Chem.*, 1907, **75**, 494). The latter ester has been prepared by condensing acetone with malonic ester in the presence of acetic anhydride and zinc chloride (Meyenberg, *Ber.*, 1895, **28**, 786), and by modifying this method we have consistently obtained yields of 50%. It has not been found possible, however, to obtain the yields of *iso*propylidenedimalonic ester claimed by Kötz, whose method is inconvenient on a large scale; yields of 10% were obtained by forming the sodiomalonic ester and carrying out the condensation in alcoholic solution in sealed tubes, but the bulk of the *iso*propylidenemalonic ester was recovered unchanged. Eventually, however, 10 g. of *iso*propylidenedimalonic ester were accumulated, but when its sodio-derivative was treated with methylene iodide, *iso*propylidenemalonic ester and a higher-boiling compound, apparently methylenedimalonic ester, resulted instead of the expected *cyclo*butane derivative. These results can be explained on the assumption that the Michael reaction is reversible (Ingold and Powell, J., 1921, **119**, 1976).

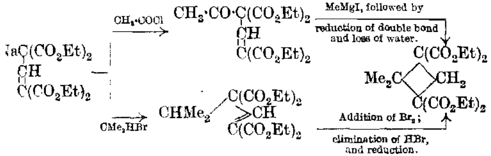
Acting on this basis, we attempted to condense methoxymethylmalonic ester with *iso*propylidenemalonic ester to give

$$CH(CO_2Et)_2\cdot CMe_2\cdot C(CO_2Et)_2\cdot CH_2\cdot OMe,$$

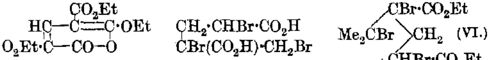
since if this ester were formed it could lose methyl alcohol with the

ɔrmation of the *cyclo*butane derivative and thus force the balanced ſichael reaction to completion. No condensation, however, could ·e effected.

It was then decided to make sodio-$\alpha\gamma$-dicarbethoxyglutaconic ster (Conrad and Guthzeit, *Annalen*, 1884, **222**, 250) the starting ·oint for the synthetic schemes :



'he first method broke down, however, for the acetyl chloride reacted ·ith the sodio-derivative in the enol phase, and the resulting *O*-acetyl ɔmpound then lost ethyl acetate to give ethyl ethoxy-α-pyrone-icarboxylate (IV), a compound previously described by Guthzeit nd Dressel (*Ber.*, 1889, **22**, 1415). Since the second part of this :heme was investigated, an account of a similar reaction with *'opropyl iodide* has been published by Hariharan, Menon, and imonsen (this vol., p. 431), but as our results throw some light ı this peculiar reaction they are worth mentioning. In addition to ıe trimesic ester obtained by these authors, it has been found that a ɔnsiderable quantity of malonic ester is present in the reaction ıixture. This result indicates hydrolysis at the double bond in the rst instance, followed by the loss of carbon dioxide as sodium ırbonate and subsequent formation of trimesic ester by the well-ıown reaction from formylacetic ester.



(IV.) (V.) (VI.)

The last line of synthetic attack to be tried was based on the ɔservation of Perkin and Simonsen (*J.*, 1909, **95**, 1169), that a *rclo*butane derivative resulted from the action of zinc and acetic ɔid on the compound (V). An attempt was made, therefore, to repare (VI) from ethyl α-acetylglutarate by the action of magnesium ıethyl iodide, followed by the replacement of the hydroxyl group y bromine, and subsequent bromination. Acetylglutaric ester has ɔw been prepared in good yield from β-chloropropionic ester and ·dioacetoacetic ester. Magnesium methyl iodide reacts, however, ith the enol phase of this ester with evolution of methane, and

α-acetylglutaric ester was recovered on acidification of the react mixture (compare Grignard, *Compt. rend.*, 1902, **134**, 849).

It was attempted to overcome this difficulty by preparing *et α-bromo-α-acetylglutarate*, but the reaction with magnesium met iodide, in which iodine was eliminated, proved to be anomalous a resulted in the reduction of the bromo-ester to α-acetylgluta ester.

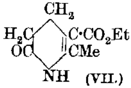
α-Acetyl-α-methylglutaric ester was then prepared in the hope th the methyl group would prevent both enolisation and reductic but on treatment with the Grignard reagent the acetyl group w eliminated to give α-methylglutaric ester (compare Grignard, *lo cit.*).

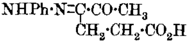
In the course of some of the above reactions it became necessa to prove the presence of α-acetylglutaric ester as an end produc and accordingly a search was made for crystalline derivatives f the purpose of characterisation. When the ester is heated wit aniline, diphenylcarbamide results, whilst treatment with gaseou ammonia in the cold in the presence of a trace of iodine gives *eth α-(α′-aminoethylidene)-glutarate*,

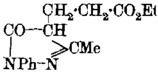
$$CH_3\cdot C(NH_2){:}C(CO_2Et)\cdot CH_2\cdot CH_2\cdot CO_2Et,$$

which on heating loses alcohol and forms the lactam (VII) (Emery *J. Amer. Chem. Soc.*, 1891, **13**, 352).

The action of benzenediazonium chloride on α-acetylglutari ester under the conditions of the Japp–Klingemann reaction gave *α-carboxypentane-γδ-dione-γ-phenylhydrazone* (VIII), whereas treatment of the ester with phenylhydrazine gave the *pyrazolone* (IX).


(VII.)


(VIII.)


(IX.)

Experimental.

αα-Dimethyltricarballylic Acid.—Acetonecyanohydrin (10 g.) (see note, this vol., p. 2629) was condensed with sodiocyanoacetic ester (from cyanoacetic ester, 12 g.) in the manner of Higson and Thorpe (*loc. cit.*). The sodio-αβ-dicyano*iso*valeric ester thus formed was refluxed with bromoacetic ester (20 g.) until neutral. Water was then added, the oil extracted with ether, the extract separated, dried, and fractionated, a considerable proportion of αβ-dicyano*iso*valeric ester being recovered unchanged, together with 2 g. of material, b. p. above 160°/14 mm. This fraction was hydrolysed by refluxing with concentrated hydrochloric acid; the solution was evaporated and the acid extracted with ether, and on evaporation of the ether

a syrup remained which partly crystallised on standing to give $\alpha\alpha$-dimethyltricarballylic acid, m. p. 149°.

iso*Propylidenemalonic Ester*.—Malonic ester (130 g.), acetic anhydride (120 g.), and a solution of zinc chloride (8 g.) in acetone (110 g.) were heated in thick sealed bulb-tubes in the water-bath for 80 hours. The reaction mixture was added to an equal volume of water and left for 24 hours with occasional shaking to decompose unchanged acetic anhydride. The ester was then separated, the aqueous layer extracted with ether, the extract added to the ester, and dried over sodium sulphate. After removal of the ether the residue was fractionated four times, giving 90 g. of *iso*propylidenemalonic ester, b. p. 116—120°/14 mm. (Found: C, 59·8; H, 8·0. Calc.: C, 60·0; H, 8·0%).

iso*Propylidenedimalonic Ester*.—*iso*Propylidenemalonic ester (20 g.) was heated in alcoholic solution with an equivalent of sodiomalonic ester in a sealed tube in a water-bath for 24 hours. The alcohol was then removed, dilute sulphuric acid added, and the separated oil extracted with ether and distilled. The distillate, b. p. above 160°/14 mm., was refractionated, yielding 3 g. of *iso*propylidenedimalonic ester, b. p. 155°/1 mm. This was refluxed until neutral with two equivalents of sodium ethoxide and excess of methylene iodide in alcoholic solution, the product poured into water, extracted with ether and fractionated; *iso*propylidenemalonic ester passed over at 100—120°/14 mm., and a small quantity of methylenedimalonic ester above 160°/14 mm., as proved by hydrolysis to an acid, m. p. 97° (glutaric acid has m. p. 97·5°).

Condensation of Sodio-$\alpha\gamma$-dicarbethoxyglutaconic Ester with Acetyl Chloride. Ethyl Ethoxy-α-pyronedicarboxylate (IV).—Sodiodicarbethoxyglutaconic ester (6 g.; vacuum-dried over sulphuric acid), anhydrous ether (20 c.c.), and redistilled acetyl chloride (2 g.) were introduced into a small flask, the neck of which was immediately sealed, and allowed to stand for 5 days with occasional shaking. The ethereal solution was then filtered from sodium chloride and evaporated on the water-bath. As the last traces of ether were being removed a distinct smell of ethyl acetate was noticed. When an attempt was made to distil the residue in a vacuum, decomposition occurred and the distillate, b. p. 180—200°/3 mm., partly solidified in the receiver. The compound crystallised from benzene–light petroleum in colourless needles, m. p. 94°, not depressed by admixture with an authentic specimen of the pyrone (IV).

Action of iso*Propyl Bromide on Sodiodicarbethoxyglutaconic Ester*.—Sodiodicarbethoxyglutaconic ester (6 g.), alcohol (20 c.c.), and *iso*propyl bromide (1·8 g.) were heated in a sealed tube at 150° for 12 hours. When the tube was opened an inflammable gas (? propyl-

ene) was evolved, and when the alcoholic solution was decant from the mixture of sodium bromide and carbonate, and a sm volume of water was added, a solid separated. This having be collected, more water was added to the filtrate. The resulti oil was extracted with ether and fractionated, giving 2 g. up 100°/3 mm., 0·5 g. from 100—180°/3 mm., and 1 g. above 180°/3 mı The last fraction partly solidified and, together with the sol collected initially, was recrystallised from alcohol and found to l trimesic ester, m. p. 131° (Found: C, 61·4; H, 6·1. Calc. f $C_{15}H_{18}O_6$: C, 61·2; H, 6·1%). On redistillation, the first fractic boiled at 80°/14 mm., and on treatment with aqueous-alcohol ammonia gave malonamide, m. p. 171°, mixed m. p. with a authentic specimen 171°.

α-Acetylglutaric Ester.—To a cooled solntion of sodium (6 g.) i alcohol (150 c.c.), acetoacetic ester (33 g.) was added, followed, afte cooling, by β-chloropropionic ester (35 g.), and the mixture wa refluxed for 3 hours on the water-bath. The excess of alcohol wa then removed, water added to the residue, and the oil extracted wit ether and fractionated; after a small quantity of acetoacetic este had passed over, ethyl α-acetylglutarate (40 g.; 70%), b. p. 145–147°/12 mm., was obtained (Found: C, 57·5; H, 8·1. Calc. fo $C_{11}H_{18}O_5$: C, 57·4; H, 7·8%), giving a deep blué coloration witl ferric chloride. In addition, a small higher-boiling fraction of ethy γ-acetylpentane-αγε-tricarboxylate passed over finally.

Action of Magnesium Methyl Iodide on α-Acetylglutaric Ester.—Th Grignard reagent from 5 g. of methyl iodide was dropped int α-acetylglutaric ester (7 g.) in ether (50 c.c.), and the mixtnre kep over-night. Dilute sulphuric acid was then added, and the ethereal layer distilled, but the ester was recovered unchanged.

α-Bromo-α-acetylglutaric Ester.—As a result of many experiment the following method was adopted as the only one to give satisfactory yields of the bromo-ester: α-Acetylglutaric ester (11·5 g.) was shaken with water (15 c.c.) and calcium carbonate (2·5 g.), and bromine was added drop by drop; the first 0·5 c.c. was rapidly absorbed, presumably by the enol phase of the ester, but further quantities of 0·5 c.c. reacted slowly, the mixture being kept cool and stirred, and the reaction appeared to be complete when 2·7 c.c. had been absorbed during the course of a week. The mixture was then extracted with ether and fractionated, the *bromo*-compound (13 g.) passing over at 162—165°/14 mm. (Found: C, 42·2; H, 5·7. $C_{11}H_{17}O_5Br$ requires C, 42·7; H, 5·5%). The compound gives no coloration with ferric chloride.

Action of Magnesium Methyl Iodide on α-Bromo-α-acetylglutaric Ester.—The Grignard reagent from methyl iodide (5·6 g.) was dropped

into α-bromo-α-acetylglutaric ester (10 g.) in ether (100 c.c.); a pale brown solid separated and the mixture was left over-night and then decomposed by adding ammonium chloride solution. The ethereal layer, which on evaporation in the cold gave no coloration with ferric chloride, was dried, the ether removed, and the residue distilled in a vacuum; iodine was evolved, and the distillate after treatment with caustic soda solution was proved to be α-acetylglutaric ester by the ferric chloride colour reaction, and by conversion into the amino-derivative (see below).

α-Acetyl-α-methylglutaric Ester.—This ester was prepared in 60% yield by the condensation of β-chloropropionic ester and methylacetoacetic ester as described above for α-acetylglutaric ester.

Action of Magnesium Methyl Iodide on α-Acetyl-α-methylglutaric Ester.—The Grignard reagent from methyl iodide (3·5 g.) was dropped into α-acetyl-α-methylglutaric ester (6 g.) in ether (15 c.c.) and refluxed for 7 hours. On being worked up in the usual manner, the main fraction boiled at 120—140°/15 mm. and redistilled at 122—125°/15 mm., and was therefore ethyl α-methylglutarate (Found: C, 59·4; H, 8·6. Calc.: C, 59·4; H, 8·9%).

Ethyl α-(α′-Aminoethylidene)glutarate.—Gaseous ammonia was passed into α-acetylglutaric ester (5 g.), containing a little iodine, for 4 days. Water separated, and on cooling, the product solidified. It was collected, dried on porous plate, and when crystallised from light petroleum (b. p. 40—60°) by spontaneous evaporation gave large colourless prisms, m. p. 37° (Found: C, 57·8; H, 8·1. $C_{11}H_{19}O_4N$ requires C, 57·7; H, 8·3%). When this compound was heated to 190—220°, alcohol was eliminated and the lactam (VIII) formed, m. p. 156° (Found: C, 58·9; H, 6·9. Calc. for $C_9H_{13}O_3N$: C, 59·9; H, 7·1%).

Action of Aniline on α-Acetylglutaric Ester.—Aniline (1 g.), α-acetylglutaric ester (2·5 g.), and a trace of iodine were heated on an oil-bath at 140—160° for 4 hours. On cooling, the product solidified, and after recrystallisation from methyl alcohol gave slightly brown needles, m. p. 238°, not depressed by admixture with a pure specimen of *s*-diphenylcarbamide.

α-Carboxypentane-γδ-dione-γ-phenylhydrazone (γδ-Diketohexoic Acid γ-Phenylhydrazone).—α-Acetylglutaric ester (4·7 g.), dissolved in a solution of caustic potash (2·4 g.) in water (9 c.c.), was kept for 24 hours in a corked flask. Water (30 c.c.), acetic acid (3 c.c.), and ice were then added, the solution was vigorously stirred, and benzenediazonium chloride (from aniline, 2 g.), together with an excess of sodium acetate, added immediately. Carbon dioxide was evolved and a flesh-coloured solid separated, which after standing over-night was collected, dissolved in sodium carbonate solution,

and boiled with charcoal. The *phenylhydrazone* was reprecipitated by the addition of hydrochloric acid, and crystallised from alcohol, giving pale yellow needles, m. p. 178° (yield 80%) (Found: C, 61·6; H, 6·0. $C_{12}H_{14}O_3N_2$ requires C, 61·5; H, 6·0%); the highly crystalline *sodium* salt is sparingly soluble in cold water.

Ethyl 1-*Phenyl*-3-*methyl*-5-*pyrazolone*-4-β-*propionate*.—α-Acetylglutaric ester (10 g.), phenylhydrazine (4 g.), and acetic acid (1 drop) were mixed and allowed to stand for 3 hours. Ether was then added and the solution dried with sodium sulphate. The ether was removed and the residue heated on the water-bath for 10 hours and then distilled, giving the *pyrazolone* as a pale yellow oil, b. p. 215°/3 mm. (Found: C, 65·7; H, 6·55. $C_{15}H_{18}O_3N_2$ requires C, 65·7; H, 6·6%).

ARMSTRONG COLLEGE,
NEWCASTLE-ON-TYNE. [*Received, July 7th*, 1928.]

NOTES.

Note on an Improved Method of Preparing Selenophen. By HENRY VINCENT AIRD BRISCOE, JOHN BUTTERY PEEL, and PERCY LUCOCK ROBINSON.

IN the preparation of selenophen by heating selenium at 400° in a current of acetylene, considerable quantities of benzene and other hydrocarbons are also formed (Briscoe and Peel, this vol., p. 1741). By the following modification, however, the proportion of these inconvenient by-products may be greatly diminished. Selenium, in portions of 5 g., is heated in an inclined Pyrex tube, closed at the lower end, and provided with an axial inlet tube delivering acetylene some inches above the selenium and well below a side tube leading to a condenser. The middle of the tube is heated to redness, and the selenium is slowly vaporised by heating it from the surface downwards. The first evidence of reaction is the flashing of the acetylene (compare Peel and Robinson, this vol., p. 2068) with deposition of carbon, and thereafter a liquid condensate is formed at the rate of 3—4 c.c. in 4 hours. As in the previous experiments, the reaction proceeds more smoothly if the selenium is mixed with the carbonaceous residue from previous runs.

About 135 c.c. of the crude brown oil thus produced were fractionally distilled through a 4-foot, glass, bead-filled column and a 1-foot, glass, spiral column for the more volatile and the less volatile fractions respectively, and yielded (i) 20 c.c. of benzene, b. p. 80°; (ii) 80 c.c. of selenophen, b. p. 110°; (iii) 10 c.c. of liquid hydrocarbons, b. p.

110—120°; (iv) 10 c.c. of liquid hydrocarbons, b. p. 150—180°; (v) 10 g. of naphthalene; and (vi) 4 c.c. of a green liquid containing selenium.

The last fraction, on microfractional distillation, gave as the middle fraction a sky-blue liquid, b. p. about 240—250°, containing about 20% of selenium, which was probably an impure specimen of selenophten, the analogue of thiophten.

Acknowledgment is made of a grant from the Research Fund of Armstrong College enabling one of us (J. B. P.) to take part in this work.—UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE. [*Received, August 10th*, 1928.]

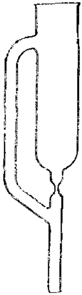
The Preparation of Acetonecyanohydrin. By KENNETH NORMAN WELCH and GEORGE ROGER CLEMO.

ACETONECYANOHYDRIN has been prepared from anhydrous hydrogen cyanide and acetone (Urich, *Annalen*, 1872, **164**, 255), and also by the action of potassium cyanide on acetone sodium bisulphite (Bucherer and Grolée, *Ber.*, 1906, **39**, 1225). The latter method is commonly given in text-books, but it has not been found possible to obtain the yields claimed, on account of the decomposition during distillation of the highly coloured, crude, reaction product. This decomposition appears to be due mainly to impurities which catalyse the following balanced reaction in the forward direction: $CMe_2(OH)CN \rightleftharpoons CMe_2O + HCN$. Moreover, a considerable amount of a solid residue always remains in the distillation flask.

The following simple method does not need anhydrous hydrogen cyanide, and is also free from the above-mentioned objection. Acetone (29 g.) is added to a solution of potassium cyanide (31 g.) in water (100 c.c.). Sulphuric acid (167 g.; 30% H_2SO_4 by weight), is then added slowly with constant stirring, the temperature being kept below 20° by the addition of ice, which also, by diluting the solution, prevents it from becoming unstirrable on account of the separation of potassium hydrogen sulphate. The reaction mixture is then extracted three times with ether, the extract dried over sodium sulphate, the bulk of the ether removed on the water-bath, and the residue rapidly distilled in a vacuum, whereupon acetonecyanohydrin (32 g.) passes over at 81°/15 mm. The compound thus prepared is much more stable than that obtained by Bucherer's method (*loc. cit.*), but even so, it is advantageous to distil it rapidly.—ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE. [*Received, July 7th*, 1928.]

Apparatus for Chromic Anhydride Oxidations. By WALLACE FRANK SHORT.

DURING the course of some experiments on the oxidation of diphenylmethane derivatives in acetic acid solution, it was found that addition of a concentrated aqueous solution of chromic acid caused the separation of unoxidised material from solution and retarded the reaction. On the other hand, addition of solid chromic anhydride resulted in poor yields of the substituted benzophenones, since they were partly destroyed under these conditions by further oxidation. Addition of an acetic acid solution of chromic anhydride produced the desired result, but the volume of the solution was inconveniently large on account of the comparatively small solubility of the anhydride. This difficulty was overcome by allowing the anhydride to dissolve in the acetic acid returning to the reaction flask from the reflux condenser. For this purpose, a modification of the apparatus designed by Walker (J., 1892, **61**, 717) for the preparation of ethyl iodide was employed. The apparatus (figured in $\frac{1}{4}$ natural size) was mounted in a cork in the flask containing an acetic acid solution of the substance to be oxidised, and was provided with a reflux condenser. The constriction n the chromic anhydride reservoir had an internal diameter of ıpproximately 2 mm., and was loosely plugged with glass wool. The ntroduction of the oxidising agent may be controlled by regulating .he boiling of the acetic acid solution in the flask.



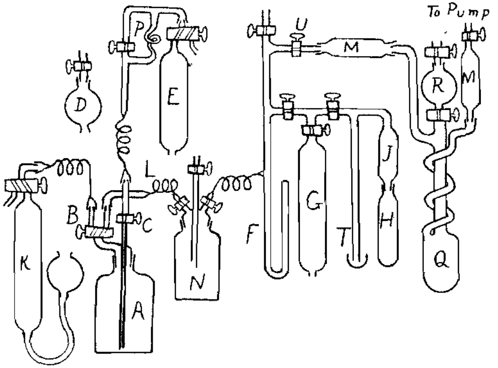
The apparatus may also be employed for the preparation of alkyl odides by Walker's method (*loc. cit.*) and for the oxidation of ›rganic substances by potassium permanganate in aqueous or acetone olution.—UNIVERSITY COLLEGE, AUCKLAND, NEW ZEALAND. [*Received, August 2nd*, 1928.]

CCCXLVI.—*The Reaction between Nitrous Acid and Hydrogen Sulphide.*

By LANCELOT SALISBURY BAGSTER.

THE precise nature of the products of reaction between nitrous acid and hydrogen sulphide solutions has not been well defined. Divers (J., 1887, **51**, 48) found ammonia and oxides of nitrogen but no hydroxylamine when a mixture of alkali nitrite and sulphide was acidified. By reaction between hydrogen sulphide and the less

FIG. 1.



soluble nitrites (such as that of silver), he obtained some hydroxylamine, an intermediate silver compound being postulated to account for its formation. A simpler explanation of this reaction is now offered.

In the course of the present work the concentration of the solutions was found to have a pronounced effect on the nature of the products, and hydroxylamine was formed under certain conditions.

EXPERIMENTAL.

In order to study the effect of very dilute nitrous acid and at the same time to obtain sufficient product for examination, an apparatus (Fig. 1) was constructed to allow of the slow passage of measured volumes of nitric oxide into a vessel containing hydrogen

sulphide solution and oxygen. The reaction vessel, *A*, of 450 c.c. capacity, was suspended on a stirrup in a thermostat at 30°, and a rocking motion was imparted to it by means of an arm projecting vertically from the stirrup and connected with a pin on a motor-driven pulley. A ground cap carried a two-way tap, *B*, for exhaustion or for admission of oxygen and hydrogen sulphide. A single-way tap, *C*, on a tube projecting into the vessel served to admit solutions or nitric oxide as required. The tube reached the bottom of the vessel for solutions, but was cut off above the liquid level for admission of nitric oxide. Connexions for transference of gases were made by flexible glass spirals with ground joints. Solutions were admitted to *A* from *D* which fitted to a double grinding on *C*.

One arm of the tap *B* led to a manometer, *F*, and a T-piece connecting with a Toepler pump and a system for generating and storing oxygen. The hard-glass tube, *H*, connected by a ground joint, contained potassium permanganate from which oxygen was generated by heat after exhaustion of the system with the mercury pump. The oxygen passed through a soda-lime tube, *J*, and was collected in the graduated holder, *G*, by displacement of mercury, the first portion generated being rejected through the mercury trap, *T*.

Nitric oxide was prepared by dropping concentrated sodium nitrite solution into a sulphuric acid solution of ferrous sulphate. The gas was passed through concentrated sodium hydroxide solution and then over solid hydroxide before collection in the graduated vessel, *E*. Glass connexions with ground joints were used. The generating apparatus was exhausted through the three-way tap on *E* and filled with nitric oxide several times before the collection of gas. The nitrite solution in the dropping funnel was exhausted to remove dissolved air.

Hydrogen sulphide was prepared by saturating magnesium hydroxide suspension in water with the gas obtained from ferrous sulphide, exhausting the solution to remove dissolved gases and then displacing the hydrogen sulphide by heat. The gas after passage through phosphoric oxide was condensed by liquid air, the container then being attached to the graduated reservoir, *K*, by a short, mercury-sealed, rubber joint, and the air removed from the container by a Geryk pump through the two-way tap. About one-quarter of the hydrogen sulphide was allowed to boil off through a mercury trap, and the gas was then collected in *K* by mercury displacement, leaving a considerable portion of residual liquid.

In carrying out an experiment, the vessel *A* was given a preliminary exhaustion by a Geryk pump through all the taps to free the barrels from air. The connecting spiral, *L*, was then fitted, and

e vessel A and the connecting leads to the oxygen reservoir :hausted by the mercury pump; 50 c.c. of water or $N/20$-hydro- .loric acid solution, previously freed from air by exhaustion in D, ›re run into A. Any trace of dissolved gas was carried over by e flow of water vapour to the phosphoric oxide tubes, MM, tached to the mercury pump. The tap B was then closed, and e pentoxide tubes allowed to absorb the water vapour in the nnecting tubes. A measured volume of hydrogen sulphide was troduced from K through a spiral which had been freed from air several alternate exhaustions and fillings with the gas. Nitrous id solutions were prepared and introduced by mixing in D under raffin oil (Taylor, Wignall, and Cowley, J., 1927, 1923) measured lumes of $N/2$-sodium nitrite and hydrochloric acid solutions, eviously freed from air by exhaustion. For nitric oxide reactions, e tap U was closed, and the connecting leads and manometer filled th oxygen from G, a measured volume of about 140 c.c. being ally introduced into A. A measured volume (about 40 c.c.) of :ric oxide was introduced through C from E through a spiral nnexion attached by the double grinding on C, and freed from air the same manner as the hydrogen sulphide connexion. The pillary spiral, P, controlling the rate of flow of nitric oxide, was ort-circuited by a tap for exhaustion of the leading tube, this being closed before gas flow started. The spiral used required iour for the passage of the 40 c.c. of nitric oxide used for a run. .e reaction vessel was kept shaken during the admission of the gas. Tests with measured volumes of nitric oxide in the absence of drogen sulphide, dilute alkali solution being used as absorbent, owed that the nitric oxide was practically all converted to nitrous d under the experimental conditions (see p. 2642). During an ual experiment, the nitrous acid, being continually removed by ction with hydrogen sulphide, would not attain appreciable icentration. For determination of the nature of the products th appreciable concentrations of nitrous acid, solutions of this ostance were run into the same apparatus in the absence of ygen.

Analysis of Products of Reaction.—(a) *Gases.* Gaseous products re collected through the mercury pump, and the procedure varied ording as nitric oxide or hydrogen sulphide was absent: in st of the runs they were not present together. (1) When nitric de was absent, nitrous oxide and excess of hydrogen sulphide re condensed in the receiver, Q, by liquid air, nitrogen and oxygen ng collected at the pump. Nitrogen was estimated by removal oxygen with phosphorus or pyrogallol. Hydrogen sulphide in was absorbed by running in alkali solution previously rendered

air-free in *R*, the taps on *MM* being closed until absorption was complete. The nitrous oxide was then collected through the pump, being identified by non-absorption in a small volume of alkaline pyrogallol, the re-kindling of a glowing splint, and combustion with hydrogen. (2) In the experiments with nitrous acid in excess of the hydrogen sulphide, the products were nitric and nitrous oxides. The former was estimated by careful addition of small volumes of pure oxygen over a small volume of alkali solution, the final excess of oxygen being removed by pyrogallol, and the residual nitrous oxide was confirmed by explosion with hydrogen. In the cases described, products remaining in solution could be determined after removal of gaseous products. (3) In reactions with nitrous acid solution and excess of hydrogen sulphide, the gaseous products contained this excess together with nitric and nitrous oxides. Alkali absorption of the hydrogen sulphide was not applicable in this case owing to reaction between the alkali sulphide and nitric oxide, and removal was effected by cupric chloride solution, blank tests having shown that a satisfactory separation was effected (see p. 2642). For solutions with excess of hydrochloric acid, the cupric chloride was added direct to the reaction vessel, a separate run being made for determination of products in solution. For reactions in absence of excess of hydrochloric acid, where residual nitrite was present in solution, the gases were expanded into the exhausted vessel *N* containing cupric chloride solution, the gases remaining after removal of the hydrogen sulphide by shaking being passed to the pump and fresh gas expanded until the reaction vessel was exhausted.

(b) *Dissolved products.* In the reaction solutions, sulphur was determined by collection on a Gooch crucible and drying at 95° (tests having shown that loss during drying did not exceed 0·5 mg.), and sulphur trioxide by barium sulphate precipitation. Sometimes colloidal sulphur passed through the Gooch crucible and was carried down by the barium sulphate; in this case, loss of sulphur by volatilisation was prevented by suspending a beaker of cold water in the mouth of the precipitation beaker, and sulphur and sulphate were determined by drying followed by ignition. Ammonia was determined by distillation into standard acid. In certain cases the nitrogen products collected did not correspond with the quantity of nitric oxide taken. Examination of these solutions (see p. 2637) showed the presence of hydroxylamine, and this was determined by titration with *N*/100-iodine solution in an aliquot portion of the filtrate from the barium sulphate precipitation in experiments where excess of hydrochloric acid was present, the acid solution being boiled again to ensure absence of traces of hydrogen sulphide.

[he iodine solution was standardised by means of a standard solu ion of recrystallised hydroxylamine hydrochloride.

For determination of hydroxylamine and sulphur products ii he absence of excess of hydrochloric acid, in which case ammoniun iitrite and sulphide were present in the solution, the combine ıydrogen sulphide was removed by adding sodium bicarbonate an passing a rapid stream of carbon dioxide for several hours. Sulphu vas filtered off, the hydroxylamine determined in a portion of th ltrate, and sulphate in the residue after acidification. Blank test vith known quantities of material showed that this procedure gav atisfactory results.

Tests showed that very nearly one-third of the hydroxylamin vas converted into ammonia during alkali distillation for ammoni stimation. This is allowed for in calculating the quantity o mmonia existing in solution.

Small amounts of nitric acid formed were estimated colori ıetrically by comparison with a standard sodium nitrate solution ıe brucine reaction being used. Nitrite was determined by reduc tion with Devarda's alloy after distillation of the ammonia, allowance being made for the small amount of nitrate.

Results are shown in Tables I and II, where volumes of gases are reduced to N.T.P., the reactions having been carried out at 30°. In each case reactions were carried out in aqueous solution (the calculated quantity of hydrochloric acid being added to the sodium nitrite when nitrous acid solutions were being prepared), and repeated with a solution of $N/20$-hydrochloric acid in the reaction vessel. The columns headed "S as SO_3" show the actual quantities of sulphur present as trioxide. In Table II, for comparison with Table I the quantities of nitric oxide that would produce the nitrous acid used if entirely converted into it are shown. On account of the less extensive reduction, it was necessary to take larger amounts of nitrous acid than correspond to the 40 c.c. of nitric oxide of Table I, but the yields have been calculated to 40· c.c. and are shown together with the actual amounts of reacting substances. In Expts. 13—16, where an excess of nitrous acid was taken, the amount consumed by reaction was calculated from the amounts of nitrogen products. If the amount of sulphur products equivalent to the nitrogen products other than nitric oxide is calculated, the residual sulphur corresponds fairly closely with the amount of nitric oxide recovered, showing that very little has been produced by direct decomposition of nitrous acid. Table I contains results for reactions with considerable hydrogen sulphide and very little nitrous acid; the opposite condition of excess of nitrous acid in quantity and low hydrogen sulphide concentration is shown in Table II

TABLE I.

Nitric Oxide–Oxygen–Hydrogen Sulphide.

(Hydrogen sulphide in excess; 225 c.c. in each case.)

Quantities of product calculated to 40 c.c. of NO.

	Expt. No.	NH_3.	NH_2OH.	N_2O.	N_2.	Free S, mg.	S as SO_3, mg.	Equivalent S, mg.	Calculated S, mg.	Oxygen used, c.c.
		Equivalent to c.c. of NO.								
HCl solution.	†1	26	9·6	0·4	1·0	146	0·3	147	147	11
	2	25	10	0·4	2·0	142	0·2	143	138	13
	3	27·5	10	0·4	0·6	150	0·1	150	155	11·5
	4	25·5	10	0·6	1·0	146	0·5	148	148	10·4
Aqueous solution.	‡*5	36		0·4	3					
	*6	34		0·4	1·5					15
	*7	34		0·4	2·5					16
	8		2·2			145	2·0	153	158	
	9		2·2			144	3·0	156	158	
Aqueous solution	10	28·5	1·7	4·1	4·6	160	2·0	168	143	16
acidified after	11	30·5	1·3	5·0	5·2	155	4·0	170	154	19
reaction.	12	27·4	2·5	4·5	6·5	153	3·0	165	145	20

* In Expts. 5—7 the quantities of product are for 40 c.c. of nitric oxide exclusive of that converted into nitrite, the amounts of which were equivalent to 21 c.c. of NO in Expt. 5, 22 c.c. in Expt. 6, and 21·5 c.c. in Expt. 7.

† HNO_3 equivalent to 0·5 c.c. NO was produced in this experiment.

‡ HNO_3 equivalent to 0·7 c.c. NO was produced in this experiment.

TABLE II.

Nitrous Acid and Hydrogen Sulphide.

		Expt. No.	NO equivalent of HNO_2 taken.	Quantities of product calculated for nitrous acid equivalent to 40 c.c. of NO. NH_3.	NH_2OH.	N_2O.	N_2.	NO.	Free S, mg.	S as SO_3, mg.	H_2S taken, c.c.
				Equivalent to c.c. of NO.							
Excess	HCl	13	224	0·2		5	1	35	15	5	58
HNO_2.	soln.	14	224	0·2		4·5	1	34	14	5	58
	Aqueous	15	224	0·15		5	1	34	17	4·5	62
	soln.	16	224	0·15		4·1	1·5	33	17	4·0	64
Excess	HCl	17	112	6·5	0·4				43	2·7	350
H_2S.	soln.	18	112	7	0·3				43	3·2	350
		19	112			10	1·5	21·5			350
		20	112			10·5	1·5	21·5			350
	Aqueous	†*21	112	8	0·8	10	1·0	25	49	1·2	350
	soln.	*22	112	7·5	0·9	10·4	0·6	26·5	46	1·3	350

* In Expts. 21 and 22 the quantities of product are for the equivalent of 40 c.c. of nitric oxide exclusive of that remaining as nitrite, the approximate amounts of which were equivalent to 4 c.c. of NO in each case.

† In Expt. 21, nitric acid was produced equivalent to 0·1 c.c. of NO.

Expts. 13—16), where the hydrogen sulphide was admitted over the water in the reaction vessel and the nitrous acid solution run in beneath the water, reaction being completed by subsequent shaking with consequent solution and oxidation of the hydrogen sulphide. Expts. 17—22 of Table II represent an intermediate condition, the hydrogen sulphide being in excess but the nitrous acid being present in quantity. In this case, the water in the reaction vessel was nearly saturated with hydrogen sulphide by admitting gas and shaking until the pressure was nearly atmospheric before addition of the nitrous acid.

For the identification of hydroxylamine, the material was prepared in greater quantity by passing rapid streams of oxygen and hydrogen sulphide and a slow stream of nitric oxide through several hundred c.c. of $N/5$-hydrochloric acid solution in a bottle carried on a shaker. After several hours, when the solution had become nearly neutral, the sulphur was filtered off, and the solution evaporated to dryness with sufficient barium chloride to precipitate all the sulphuric acid. The residue was extracted with absolute alcohol, the extract evaporated, the crude residue extracted with alcohol–ether, and the solvent again removed. The resulting white solid reduced iodine solution and Fehling solution (Found: Cl, by $AgNO_3$ titration, 52·4. Calc. for NH_2OH,HCl, 51·1; for NH_4Cl, 66·4%); 0·014 g. required 58 c.c. of iodine solution, 29 c.c. of which were equivalent to 10 c.c. of $M/100$-hydroxylamine solution (Calc. for NH_2OH,HCl, 58·4 c.c.).

Discussion.

Considering first the nitrogen products, it will be seen from Table II that when the nitrous acid is in excess and the hydrogen sulphide concentration relatively small (Expts. 13—16) very small amounts of hydrogenated nitrogen compounds are formed (the very small quantities of ammonia were determined by Nessler solution), nitric oxide and smaller amounts of nitrous oxide being the principal reduction products. When the hydrogen sulphide is in excess, however, and the nitrous acid concentration is very small (Table I) the reduction is almost entirely to hydrogenated products, ammonia and hydroxylamine in acid solution, and chiefly ammonia with a smaller proportion of hydroxylamine in aqueous solution.

In the presence of excess of oxygen, nitric oxide would be reconverted into nitrous acid, and a catalytic effect would be apparent from a greater quantity of sulphur products and greater oxygen consumption; but it can be shown from Expts. 1—4, 8, and 9 that there has been no such catalytic effect. In the tables, the quantities of sulphur found as trioxide have been multiplied by 4 to give the quantity of free sulphur that would have been produced by a corre-

sponding amount of *oxidation*, and the *equivalent quantity* of free sulphur added to the actually determined free sulphur is given in the column "Equivalent S." The column "Calculated S" shows the amount of sulphur corresponding to the oxidation equivalent of the various nitrogen products collected. As the calculated and the equivalent sulphur correspond, reduction to the nitrogen products found must have been direct without intervening formation of nitric oxide. The quantities of oxygen consumed in Expts. 1—4 are also very close to the 10 c.c. required for direct formation of nitrous acid from 40 c.c. of nitric oxide, further re-formation of which would consume more oxygen. The greater quantity of oxygen consumed in Expts. 6 and 7 is discussed later.

The most noteworthy product is the hydroxylamine, which i destroyed by reaction with nitrous acid. Its formation and sta bility during reduction of very dilute nitrous acid solution are prob ably due to the fact that each molecule of the acid is reduced by th excess of hydrogen sulphide before it has opportunity to react wit hydroxylamine. The production of the compound by Divers (*loc cit.*) may be similarly explained, for the effect of hydrogen sulphid on a *slightly soluble salt in suspension* would be to produce a sma *concentration of nitrous acid which would be continually remove by the hydrogen sulphide.*

When the addition of nitric oxide is effected in the absence hydrochloric acid, there is still only a very small yield of gaseo products, but ammonia is the principal reduction product, t quantity of hydroxylamine being smaller than in acid solutio but, as shown in Expts. 5—7, a proportion of the nitrous acid h formed ammonium nitrite which has not had time to react wi the hydrogen sulphide—it will be shown later that this reaction very slow (p. 2639).

The result of acidifying the solutions containing nitrite is sho in Expts. 10—12 (Table I), where hydrochloric acid was added aft addition of nitric oxide. The calculated quantity of sulphur smaller than the sulphur found, whilst the oxygen consumption greater than in Expts. 6 and 7, where no acid was added af reaction. Evidently, the nitrous acid set free on addition hydrochloric acid had sufficient concentration to form some nit oxide and thus, to a small extent, to act catalytically. The re tively considerable amounts of nitrogen and nitrous oxide must a have been produced during the reaction after acidification, very lit being obtained in Expts. 5—7.

Considering next the sulphur products, it will be seen that, exc in the case where nitrous acid is present in quantity and in exc the hydrogen sulphide *concentration* being small (Expts. 13—1

the greater proportion of the hydrogen sulphide is oxidised to sulphur with a relatively small amount of sulphur trioxide. Expts. 17—22 show that, even when nitrous acid solution of appreciable concentration is added to a fairly concentrated hydrogen sulphide solution, the sulphur predominates.

In the hope of obtaining further information as to the nature of the processes involved, the reaction between hydrogen sulphide and ammonium nitrite was investigated. In Table IIIA is shown the result of passing hydrogen sulphide continuously through an approximately *N*/20-solution of ammonium nitrite (prepared from silver nitrite and ammonium chloride). There was gradual reduction of nitrite, chiefly, but not completely, to ammonia, about 50% being reduced in 24 hours. The sulphur produced was partly precipitated and partly dissolved as yellow polysulphide. The slow reaction when compared with the extremely rapid oxidation with free nitrous acid suggests that the free acid produced in the present case by hydrolysis is the active agent, and not the nitrite ion which is now present in quantity. The solutions saturated with hydrogen sulphide had a very feebly acid reaction, which diminished as the ammonium sulphide increased; p_H values determined by a comparator with phenol-red are shown. In order to study the effect of sulphide-ion concentration, the experiment was repeated with addition of sufficient ammonium sulphide to make the solution *N*/6 with regard to ammonia. The result of passing a continuous stream of hydrogen sulphide through this mixture is shown in Table IIIB. The reaction, at first slower than in the absence of excess of sulphide, accelerated considerably after a few hours. The sulphur produced dissolved, forming a yellow polysulphide solution.

TABLE III.

Hydrogen Sulphide and *N*/20-Ammonium Nitrite.

(25 C.c. samples.)

A. Nitrite + H_2S.

Time (hrs.)	0.	½.	3.	6.	9.	12.	27.	32.
C.c. of *N*/10-HCl for NH_3 ...	12·2	12·5	13	13·7	14	14·3		16
C.c. of *N*/10-HCl for HNO_2	12·0	11·5	10·9	10	9·4	8·9	6·1	5·5
p_H			6·0			6·3		6·6

B. Nitrite + H_2S + *N*/6-NH_4HS.

	(1)					(2)		
Time (hrs.)	0.	3¼.	6.	8.	11.	0.	1½.	3½.
C.c. of *N*/10-HCl for HNO_2	12	11·5	8·5	5	2·3	12	11·8	11·3

C. Nitrite + H_2S + *N*/6-Polysulphide.

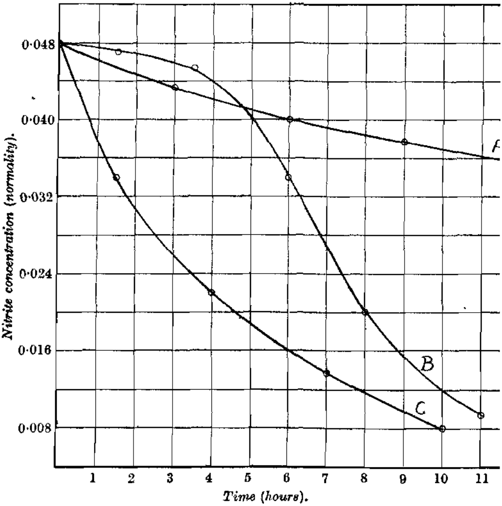
Time (hrs.)	0.	1½.	4.	7.	10.
C.c. of *N*/10-HCl for HNO_2 ...	12	8·5	5·5	3·4	2·0

Table IIIc shows the result of adding ammonium sulphide ai sulphur, forming polysulphide, at the commencement of reactio It will be seen that the reaction is rapid from the beginning. T results shown in Table III are plotted in Fig. 2.

N/6-Ammonium sulphide solution saturated with hydrog sulphide has a slightly alkaline reaction, p_H 7·2—7·3 by comparatc

FIG. 2.

A = *Nitrite.* B = *Nitrite + sulphide.* C = *Nitrite + polysulphide.*



Hydrogen sulphide and ammonium nitrite.

and the polysulphide solution has a value of the same order. Tl very slow reaction with considerable ammonium hydrosulphide i solution is probably due to diminished nitrous acid concentratic owing to smaller hydrogen-ion concentration. The increased rat when sulphur is formed or added in sufficient quantity may t ascribed to the influence of polysulphide ion. Although Küst (*Z. anorg. Chem.*, 1905, **44**, 431) has shown by *E.M.F.* measuremen in·t these ions have a smaller reduction tendency than the sulphic the

on, he has also found (*ibid.*, **43**, 53) that, as the proportion of ulphur increases, the hydrolysis of sodium polysulphide diminishes, hus indicating greater strength for the acid. In the solutions now nder consideration, which were saturated with hydrogen sulphide, he principal constituents would be NH_4HS and NH_4HS_x, and the rincipal ions $NH_4^{\cdot}$ and HS' in one case, and $NH_4^{\cdot}$ and HS_x' in the ther. The polysulphide will be less hydrolysed and more dis-ociated, and the HS_x' ion will be present in greater quantity than he HS' ion in the absence of sulphur; thus a considerable increase n concentration of the reducing ion will be caused by the presence f sulphur dissolved as polysulphide. This in turn may lead to nore rapid reaction.

The last experiments thus afford some evidence that the reaction etween hydrogen sulphide and nitrous acid is between the undis-ociated acid and the sulphide ion. It may be suggested that the rimary reactions are of simple type, and that nitric and nitrous xides and nitrogen are secoudary products. With appreciable oncentration of nitrous acid, the reactions

$$(1)\ 3HNO_2 + S'' \longrightarrow 3HNO + SO_3(+ 3H_2O)$$

nd

$$(2)\ HNO_2 + S'' \longrightarrow HNO + S\ (+ H_2O)$$

nay be expected. The proportions in which reactions (1) and (2) ccur would largely depend on the relative concentrations of the eacting substances. Reaction of the hyponitrous acid with more itrous acid would yield nitric oxide. Direct decomposition of yponitrous acid has been shown to yield nitrous oxide and nitrogen Divers, J., 1889, **55**, 112). The nitric oxide and some of the itrogen and nitrous oxide found in various experiments may thus e accounted for, a portion of the nitrous oxide and nitrogen prob-ably being formed as secondary products of reaction (3) (helow). With smaller concentration of nitrous acid and considerable hydrogen ulphide concentration, reactions

$$(3)\ HNO_2 + 2S'' \longrightarrow NH_2OH + (H_2O) + 2S$$

nd

$$(4)\ HNO_2 + 3S'' \longrightarrow NH_3 + (2H_2O) + 3S$$

ay be expected, with the possibility of more nitrous oxide and erhaps nitrogen being formed by reaction between nitrous acid nd hydroxylamine.

In the present work the slow addition of nitric oxide to the ystem would produce an exceedingly small concentration of nitrous cid which would not increase, owing to reaction with hydrogen lphide, and secondary reactions with nitrous acid would not he xpected to occur to any extent. Reactions (3) and (4) appear to ave proceeded together in Expts. 1—4 in the presence of excess of

hydrochloric acid, whilst in absence of acid (Expts. 5—9) reaction (4) predominates. Two causes may be suggested to account for this variation: (1) A reduced free nitrous acid concentration owing to nitrite formation and reduction of hydrogen ion through the presence of hydrolysed ammonium sulphide—it does not seem likely, however, that variation in an already very small concentration of a substance taking a unimolecular part in a reaction would appreciably alter the nature of the reaction in the presence of considerable excess of the second reactant. (2) Variation of sulphide-ion concentration is probably of greater importance; this concentration, very small in hydrochloric acid solution, will be much greater in presence of ammonium sulphide, thus favouring reaction (4).

In Table II there is no definite difference between the products in Expts. 15 and 16 with only nitrous acid, and those in Expts. 13 and 14 with excess of hydrochloric acid. This is to be expected on account of the considerable amount of sulphuric acid produced. Small variations between products in Expts. 17—20 and Expts. 21 and 22 with excess of hydrogen sulphide may be due to variation in acidity, as only small amounts of sulphuric acid were produced. Considerable variation is not to be expected, as the solutions would in all cases remain acid until most of the nitrous acid was destroyed.

A blank test with hydrogen sulphide, oxygen, and an amount of ammonia equal to that present as sulphide at the end of reaction, yielded in the absence of nitric oxide about 4 mg. of free sulphur and 0·3 mg. as trioxide in ½ hour. As the average ammonia concentration during a run would be much less than the maximum, the amount of sulphur formed by direct oxidation in Expts. 10—12 would be very small. The greater oxygen consumption in Expts. 6 and 7 than in Expts. 1—4 may be due to this small direct oxidation.

The following are results of some other blank tests.

(1) Absorption by copper chloride of hydrogen sulphide from mixture with nitric oxide:

100 c.c. of H_2S + 38 c.c. of NO taken; 37·5 c.c. of NO recovered.

(2) Absorption by alkali solution of nitric oxide (41 c.c.) from mixture with oxygen (10 c.c.):

$KMNO_4$: required 36·9 c.c.; calculated 36·7 c.c.

(3) Estimation of nitrite in ammonium nitrite solution containing polysulphide: 25 C.c. of *N*/20-ammonium nitrite solution were added to concentrated alkali and the ammonia was distilled off. The nitrite was then reduced by Devarda's alloy and the resulting ammonia required 12·0 c.c. of *N*/10-HCl. The process was then repeated with a fresh sample containing the amount of polysulphide used in the experiments of Table IIIc, and 11·9 c.c. of acid were

required. There has evidently been no appreciable reduction of nitrite in the strongly alkaline solution during the time required for preliminary distillation of the ammonia.

(4) In view of the fact that hydroxylamine is known to act as an oxidising agent under certain conditions, the possibility of its reacting with hydrogen sulphide in presence of ammonium sulphide and sulphur was tested under various conditions. It was found that no measurable loss of hydroxylamine occurred in dilute solutions in an hour.

Summary.

The products of reaction of nitrous acid solution with hydrogen sulphide vary with relative concentrations. With appreciable concentration of nitrous acid, the reduction products are chiefly nitric and nitrous oxides; with small concentrations of nitrous acid, they are ammonia and hydroxylamine, the proportions of which vary according to the concentration of sulphide ion in solution.

A series of simple reactions is proposed, nitric and nitrous oxides being regarded as products of hyponitrous acid formed primarily.

The proportion of sulphur trioxide to free sulphur is small even with fairly concentrated nitrous acid solutions unless the hydrogen sulphide concentration is small.

Hydrogen sulphide reacts slowly with ammonium nitrite, converting it into ammonia. The rate of reaction is diminished by addition of ammonium sulphide and increased by addition of polysulphide. A suggested explanation is based on the fact that the polysulphide ion is known to be more acidic than the sulphide ion and would thus furnish a greater concentration of reducing ions in solution.

THE UNIVERSITY OF QUEENSLAND,
BRISBANE. [*Received, July 18th*, 1928.]

CCCXLVII.—*The Velocity of the Acid Hydrolysis of Cotton Cellulose by Hydrochloric Acid, Alone, and in Presence of Alkali Chloride.*

By EDWARD HUNTER.

IT has been shown by Åkerlöf (*Z. physikal. Chem.*, 1921, **98**, 260) that the velocity of hydrolysis of ethyl acetate by hydrochloric acid in presence of large concentrations of neutral salt is a function of the activity of the hydrogen ion, irrespective of the kation of the added chloride.

The work here described was undertaken to determine whether

the principles of activity could be extended to a heterogeneous reaction catalysed by hydrogen ions. The reaction chosen is the hydrolysis or "modification" of cotton cellulose in hydrochloric acid both alone and in presence of potassium, sodium, and lithium chlorides. With dilute acid the ultimate reaction product is hydrocellulose, a solid adhering to the unchanged cotton. According to Wohl and Blumrich (*Z. angew. Chem.*, 1921, **34**, 17), this substance is a reversion product of dissolved reducing sugars (primary products of reaction) and some undissolved substance in the solid cotton. They observe that hydrocellulose is much more difficult to hydrolyse than cellulose, but it should be borne in mind that hydrolysis can be effected by prolonged heating with very concentrated acid.

EXPERIMENTAL.

Methods of Hydrolysis and Analysis.—The hydrolyses were carried out by adding 70 c.c. of the acid solution to a weighed quantity of cotton (about 2·7 g.), stirring to remove air bubbles, and immersing the reaction vessel in the thermostat. For potassium chloride and some lower concentrations of sodium chloride the vessel was a tightly-corked flask, but it was found advisable to carry out the other reactions in sealed glass tubes.

After hydrolysis the cotton was washed by water with suction, and its copper number determined by Brady's method (see also Clibbens and Geake, *Shirley Institute Memoirs*, 1924, **2**, 387). Two corrections were applied in the calculation. (1) The moisture content of the original cotton was determined by heating 1 g. samples, loosely packed in weighing bottles, at 105° to constant weight. (2) The copper number of unmodified cotton (mean of several determinations) was subtracted from the value found after hydrolysis.

When a sample of cotton was steeped in acid, the concentration of acid slowly decreased by a slight amount until an equilibrium was reached after about 2½ days:

Time (hrs.)	0	4·75	27	64·3
Acid concentration, *N*	0·100	0·0992	0·0983	0·0980

The fall in concentration in 60 hrs. of several concentrations of acid was measured:

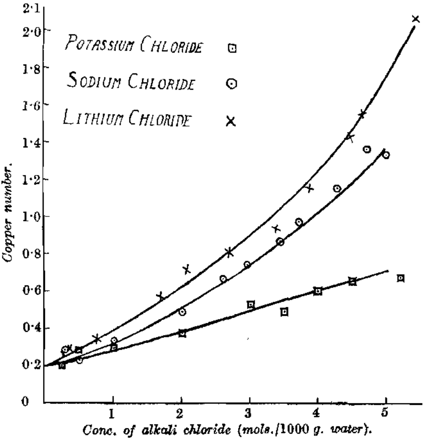
Original concentration	0·869	0·435	0·244	0·0871
Final concentration	0·866	0·433	0·242	0·0855
Fall, %	0·35	0·46	0·8	1·8

This change in concentration is ascribed to imbibition of acid by the cotton, and it has been ignored in the velocity measurements.

For the velocity of the hydrolysis (by acid of constant concen-

tration), Birtwell, Clibbens, and Geake (*J. Textile Inst.*, 1926, **17**, T161) have submitted the formula $N_{Cu} = KT^{0 \cdot 6}$, where N_{Cu} is the copper number, K a velocity coefficient, and T the time of reaction in days. The results of these authors show that K is only constant within 5—10%. Furthermore, the index here given as 0·6 apparently varies with the type of cotton. For these reasons, in the present work, reaction velocities are compared by carrying out the acid steeping for exactly the same length of time in all cases, a period of 3 days at 40° being chosen as most suitable.

FIG. 1.

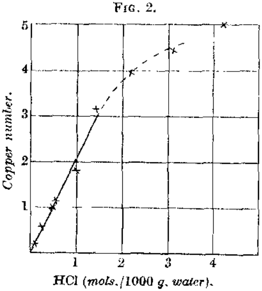


N/10-Acid (0·1 mol. per 1000 g. of water) was prepared by dilution of standard hydrochloric acid made by the method of Hulett and Bonner (*J. Amer. Chem. Soc.*, 1909, **31**, 390). The acid–alkali chloride mixtures were prepared by adding weighed amounts of salt to a known weight of acid. In the lithium chloride series the concentrations of acid and chloride were checked by analysis.

Results.—In Fig. 1 the copper numbers for the 3-day hydrolysis at 40° are plotted against the concentrations (x) of neutral salt in the mixture $0 \cdot 1HCl + xRCl + 1000$ g. H_2O; and Fig. 2 shows the results for pure acid of varying molality.

The last three results in the acid series do not represent the t velocity values for the corresponding molalities of acid.] reasons can be given for this. (1) Hydrolysis with such strong a for 3 days resulted in a complete change of form of the cottor short thread-like particles, in place of the interwoven fibres after more moderate modification; hence it seems likely that hydrocellulose itself was partly decomposed by the acid. (2) determining the copper number of such highly modified cot samples, the amount of copper solution used in the standard metl was insufficient, and it was therefore necessary to use a lar quantity, thereby deviat from the rigid conditi prescribed for the method

FIG. 2.



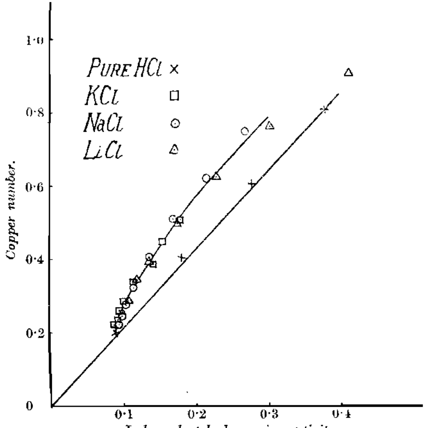
It is obvious from diagrams that no great qu titative accuracy can claimed for the veloc measurements. The sou of the largest error is alm certainly in the process hydrolysis, for two samp of cotton of equal weig cannot be expected to of the same surface area the solution. However, t results clearly show t qualitative effects upon t reaction velocity of adding alkali chloride to $N/10$-hydrochloric aci

The curves of Fig. 1 resemble those connecting molality of add chloride with hydrogen-ion activity in solutions of the type use This suggests a connexion between hydrolysis velocity and tl hydrogen-ion activity of the acid solutions. The curves in Fig. have been obtained by plotting Harned's values for hydrogen-io activity in solutions of this type (*J. Amer. Chem. Soc.*, 1920, 4; 1808) against the copper numbers for corresponding molalities, a read off from Figs. 1 and 2. Harned's data refer to 25°, but only small error is introduced by applying them to 40°.

It will be seen from the diagram that in pure acid there is a simpl direct proportionality between hydrogen-ion activity and coppe number (velocity of reaction) for activities of the same order a those of the acid–alkali chloride series. No such simple relatio exists for the acid–salt mixtures. Plotted separately, the result for each series give a smooth curve. The three curves are prac tically coincident near their origin, and are only slightly divergen

with increasing molality. In Fig. 3 a single curve has been drawn for the three series; this originates on the pure acid curve at the hydrogen-ion activity of $N/10$-acid, and then rises above it. Since Harned's values are limited to solutions which are not stronger than $3M$ with respect to added chloride, the ultimate trend of the activity–velocity curves has to be left undefined—they may either become parallel to the pure acid line or intersect it at very high values of the hydrogen-ion activity.

Fig. 3.



For the range examined, the notable fact is that, of two solutions having the same hydrogen-ion activity, that with neutral salt present gives a higher reaction velocity than that with acid alone. In attempting an explanation of this fact, it seems natural to assume that reaction occurs between dissolved reactants in a thin layer of solution touching the surface of the solid cotton; in these circumstances Brönsted's equation (*Z. physikal. Chem.*, 1925, **115**, 337) can be expected to hold, *viz.*, $v = ka_A a_B/f_X$, where v is the velocity, k a velocity coefficient, a_A and a_B are the activities of the reactants, and f_X is the activity coefficient of the "critical complex." If the reaction be written as $H^{\cdot},H_2O$ + Cellulose ⟶ [(Cellulose),$H^{\cdot},H_2O$] ⟶ Hydrocellulose + $H^{\cdot}$, one obtains the expression $v = ka_H a_C/f_X$,

a_H and a_C being the respective activities of the hydrogen ion an the neutral cellulose, and f_X having its former significance. Sinc the cellulose is a neutral molecule, the expression can he modifie to $v = ka_Hc/f_X$, where c is the concentration of cellulose. Apa from the independent hydrogen-ion activity, the important varian in this expression is f_X, for the critical complex is a charged molecule the activity coefficient of which may be expected to he very respon sive to changes in the activities of the other reactants. Now, fo similar hydrogen-ion activity, the saline solutions have a far greate molality of electrolyte than the salt-free solutions. In Fig. 3 th highest molality of pure acid is 0·5, whilst that of the acid–chlorid solutions reaches 3·1. Hence any effect upon the activity coefficien of the "critical complex" with increasing molality of electrolyt will be shown to a more pronounced degree in the latter type o solution. The relative form of the activity–velocity curve for suc solutions and for salt-free solutions is explained if it is accepted that addition of large quantities of electrolyte to the solution lowers f_X, for the velocity of the reaction is inversely proportional to this activity coefficient. The gradual divergence of the activity–velocity curves for the three different chlorides can then be ascribed to slight differences in the quantitative effects of each salt on the "critical complex."

The author's thanks are due to Professor A. J. Allmand, under whose direction the work was carried out, and to Dr. D. A. Clibbens, who supplied the cotton and gave very helpful advice.

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King's College. [*Received, May 23rd, 1928.*]

CCCXLVIII.—*Cobalt Allylamines: A Supposed Co-ordination Number of Eight for Cobalt.*

By William Ralph Bucknall and William Wardlaw.

From a careful survey of the chemical evidence, Sidgwick ("The Electronic Theory of Valency," p. 152) has concluded that up to the end of the first long period in the classification of the elements the highest covalency of an atom is six. He also states (*op. cit.*, p. 160) that "it should he noted that there are a certain number of compounds which appear to indicate values of the covalency in excess of those allowed by the rule. In none of these have the structure and molecular weight been definitely ascertained." There are recorded in the literature, however, the preparation and

properties of an interesting complex salt of cobalt, which is mentioned by Weinland ("Komplexverbindungen," 1919, p. 13) as an example of a co-ordination number of eight for cobalt, instead of the usual six anticipated from Sidgwick's rule. The substance in question was prepared by Pieroni and Pinotti (*Gazzetta*, 1915, **45** ii, 100), who found that when dry air was drawn through a saturated solution of cobaltous chloride (dried at 140°) in absolute alcohol to which dry allylamine had been added there separated a red, crystalline compound. It dissolved in cold water with the production of a neutral solution, and from cryoscopic molecular-weight determinations it was concluded that in aqueous solution the substance dissociated into a maximum of four ions. From these data and the percentages of cobalt and chlorine found in the compound, Pieroni and Pinotti assigned to the new substance the formula $[Co,8C_3H_5\cdot NH_2]Cl_3$. Later, however, Pieroni (*ibid.*, 1921, **51**, i, 42) reinvestigated the reaction and, as a result of a more complete analysis, deduced the new formula

$$\left[Co\begin{matrix}6C_3H_5\cdot NH_2\\ 2O_2\end{matrix}\right]Cl_3,H_2O_2.$$

On titration with permanganate, the titre was in excess of that demanded by the unsaturated amine, and it was suggested that the excess was required by the hydrogen peroxide present in the molecule. As both formulæ assign a co-ordination number of eight to the cobalt and the reaction appeared to have several unusual features, it seemed of interest to reopen the investigation.

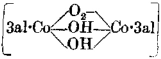
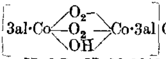
EXPERIMENTAL.

Preparation of Hexa-allylamineperoxodihydroxodicobalt Trichloride,* $\left[3al\cdot Co\begin{matrix}O_2\\ OH\\ OH\end{matrix}Co\cdot 3al\right]Cl_3$.—To a saturated solution of cobaltous chloride (10 g.; dried at 140°) in 100 c.c. of water-free alcohol, dry allylamine (32 g.) was added in portions, with constant shaking, air being displaced by a current of nitrogen; considerable heat was evolved and the solution became reddish-blue. On cooling, purplish-red, needle-like crystals separated in good yield. They were very deliquescent and unstable, allylamine being readily liberated. With alcohol, the crystals gave a blue solution, and in water they underwent decomposition, cobalt hydroxide being precipitated almost immediately. Pieroni assigned to these crystals the composition $CoCl_2,3C_3H_5\cdot NH_2$. When a current of dry air was passed through the reaction flask containing the crystals in contact with their mother-liquor, the

* al = $C_3H_5\cdot NH_2$.

solution changed in colour from purplish-red to brownish-red, and minute red crystals slowly separated. After oxidation for about 3 days, these crystals were collected, washed with absolute alcohol (in which they are insoluble) until the filtrate was colourless, and then air-dried on a porous plate. In the first attempts to obtain this oxidised product, cobalt hydroxide separated after the oxidation had proceeded for a short time. This was apparently due to the presence of moisture in the alcohol, for this difficulty did not arise when the solvent had been refluxed and distilled twice over barium oxide and twice over calcium turnings before use. The allylamine for the early experiments was prepared by the method of Pieroni and Pinotti (*Gazzetta*, 1915, **45**, i, 100), but later, purchased samples were dried by two distillations over sodium and then had b. p. 55°.

Analysis.—The cobalt was estimated as sulphate by gentle ignition of the substance with sulphuric and nitric acids in an air-oven. For the estimation of the chlorine, cobalt was removed as hydroxide by addition of sodium hydroxide to a solution of the substance, and the chloride then precipitated as silver chloride [Found: Co, 18·6; Cl, 16·7; C, 33·6; H, 6·7; N, 13·1.

 Cl_3 (I) requires Co, 18·65; Cl, 16·8; C, 34·1; H, 7·0; N, 13·3%.  Cl_3 (II) requires Co, 18·2; Cl, 16·45; C, 33·4; H, 6·7; N, 12·9%]. From the analytical results, formula (I) seems the more probable.

Molecular-weight Determinations.—The molecular weight was determined by the depression of the freezing point of water. If either of the above-mentioned formulæ represents the correct formulation, then four ions should be present in solution and the apparent molecular weight, when ionisation is complete, should be *ca.* 160. The results in Table I, calculated for formula (I), furnish evidence in favour of such a formulation.

TABLE I.

G. of substance per 100 g. water.	Conc. (mols. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
1·022	0·01616	3·60	176·0
1·159	0·01833	3·46	182·7
1·736	0·02744	3·11	203·0

Molecular-conductivity Determinations.—The molecular conduct- was determined at various dilutions at 0°. Table II gives recorded of μ for the complex chloride, and for comparison the

values of the molecular conductivities of typical salts at 0° are given in Table III.

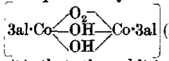
TABLE II.

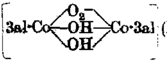
v (litres/mol.)	45·6	65·9	131·8	263·6	527·2	730·0
μ	119	128·8	144·3	159·3	176·3	184·8

TABLE III.

v (litres/mol.)	32	64	128	256	512	1024	
$K_3Fe(CN)_6$	215	227	243	254	264	282	
$K_3W(CN)_8$	211	224	238	250	259	264	
$AlCl_3$						226	(approx.)
K_2SO_4					*158*	*161*	

From the results given in Table II, μ_∞ for the complex chloride is estimated to be *ca.* 210. Although the values of μ for the complex salt are less than would be expected for a normal four-ion compound, they are nevertheless in accord with the formula if we assume that the large complex ion is slow-moving, as is frequently the case. Since λ_∞ for Cl′ at 0° is *ca.* 46, then by Kohlrausch's law the ionic mobility of the complex ion is approximately 70, the usual figure for a tervalent ion being about 110.

Preparation of Hexa-allylamineperoxodihydroxodicobalt Trinitrate,

$(NO_3)_3$.—Pieroni and Pinotti noticed (*loc. cit.*) that the addition of nitric acid to a concentrated aqueous solution of the complex chloride produced red, acicular crystals, which were not further investigated. It has been found, however, that the addition of either nitric acid or a solution of any metallic nitrate will cause precipitation of a red compound. This new substance thus appears to be the result of an ionic reaction between the complex chloride and the nitrate ion.

The compound was prepared by the addition of about 1 c.c. of pure nitric acid to 20 c.c. of a solution of the complex chloride (2 g.), and was freed from acid by washing with cold water, in which it is slightly soluble; the filtered substance was air-dried on a porous plate. It contained no chlorine, and when it was moistened with sulphuric acid, nitric acid was liberated. It was slightly soluble in cold water, and on standing or by warming, hydrolysis occurred with the precipitation of hydroxide. Warming with sodium hydroxide caused the evolution of allylamine, and by distillation with sodium hydroxide and Devarda's alloy the nitrate groups were reduced to ammonia, which was titrated together with the liberated allylamine (Found: Co, 16·6; N, 17·8; N : Co = 9·03 : 2.

$(NO_3)_3$ requires Co, 16·6; N, 17·7%).

The nitrate hydrolyses in boiling water, but the presence c nitric acid prevents decomposition. Pieroni and Pinotti (*loc. cit* remarked on the formation of a yellow substance together with heavy red compound when the complex nitrate was boiled wit dilute nitric acid. It has been found, however, that the onl product of this reaction is a red precipitate of the same compositio as the above nitrate. It appears that the presence of the nitri acid merely retards the hydrolysis, and possibly decreases th solubility of the complex nitrate. If the concentration of th nitric acid is too high, the salt is dissolved and the complex ion i apparently destroyed.

Reactions of the Complex Salts.—Concentrated hydrochloric aci gives, with either of the complex salts, a dark green, insolubl substance, which on warming dissolves to a bluish-green solutio of cobaltous chloride and allylamine hydrochloride. The additio of concentrated hydrochloric acid to an aqueous solution of th complex chloride produces a green solution which reverts to th blue colour of cobaltous chloride only on warming. Sulphuric aci decomposes the complex ion and forms cobaltous sulphate. Wit silver nitrate solution, the complex chloride gives an immediat precipitate of silver chloride, together with a red precipitate, i concentrated solutions, of the complex nitrate. Ammoniun sulphide immediately precipitates the cobalt as sulphide. Th complex salts react, on warming, with potassium iodide solutio with the liberation of iodine; with potassium bromide, however no oxidation could be detected.

Discussion of Results.

The most important result of this investigation has been t indicate a new formulation for the salts originally prepared b Pieroni and Pinotti. The analytical data now obtained are com pared below with those previously recorded for the complex chloride

	Co.	Cl.	N.	C.	H.
Pieroni and Pinotti	9·7	17·4			
Pieroni	10·0; 9·25	17·1	13·7	35·76	7·76
Present authors	18·6	16·7	13·1	33·57	6·71

Our percentages for Cl, N, C, and H are of the same order as those determined by Pieroni and Pinotti for this compound, but there is a marked difference in the percentages of cobalt. Whereas the analytical figures of Pieroni and Pinotti indicate a ratio of Co : Cl = 1 : 3, the new figures show a ratio of 2 : 2·982. Such a ratio would be anticipated from the results obtained by Werner from the oxidation of ammoniacal solutions of cobaltous salts. He was

able to isolate and examine many new substances which he formulated as bridge compounds ("Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie," 1920 ed., pp. 293 *et seq.*); for example, *one of the first products of the atmospheric oxidation* of ammoniacal cobalt solutions is a brownish-black oxy-compound of the composition $[(NH_3)_5Co^{III}\cdot O_2\cdot Co^{III}(NH_3)_5]X_4$, which on further oxidation yields the intensely dark green, so-called anhydro-oxy-cobaltate, $[(NH_3)_5Co^{III}\cdot O_2\cdot Co^{IV}(NH_3)_5]X_5$. Other products obtained by similar means include $\left[(NH_3)_4Co^{III}\begin{smallmatrix}OH\\OH\end{smallmatrix}Co^{III}(NH_3)_4\right]X_4$, the melano-chloride $\left[\begin{smallmatrix}(NH_3)_3\\Cl_2\end{smallmatrix}Co^{III}\cdot NH_2\cdot Co^{III}\begin{smallmatrix}(NH_3)_3\\Cl_2\end{smallmatrix}\right]X$, and also the three-bridge compound, $\left[(NH_3)_3Co^{III}\begin{smallmatrix}NH_2\\O_2\\OH\end{smallmatrix}Co^{IV}(NH_3)_3\right]X_3$. From the melano-chloride by simple reactions the compound

$$\left[(NH_3)_3Co^{III}\begin{smallmatrix}NH_2\\OH\\OH\end{smallmatrix}Co^{III}(NH_3)_3\right]X_3$$

can be prepared.

The possibility that the compounds $\left[3al\cdot Co\begin{smallmatrix}O_2\\OH\\OH\end{smallmatrix}Co\cdot 3al\right]X_3$ would result from the reactions dealt with in the present investigation is therefore not unexpected. The reaction is in accordance with the general tendency of alkaline solutions of cobaltous salts to produce polynuclear complex compounds on atmospheric oxidation. The new formulation assigns to cobalt valencies of three and four. Although quadrivalent cobalt is not normally considered to exist, yet Werner found it necessary to postulate its presence in such polynuclear compounds as those mentioned above. Moreover, it will be noticed that this formula assigns to cobalt the normal covalency of six, and there is no evidence that Pieroni and Pinotti's compounds necessitate any modification of Sidgwick's rule.

It is interesting to compare the results obtained from nickel salts under similar conditions. Pieroni and Pinotti (*Gazzetta*, 1914, **44**, ii, 366) found that by the action of allylamine on various nickel salts, several substances could be prepared which, like the compound of cobaltous chloride with allylamine, were very unstable, hydrolysing immediately in water. They concluded that in no case was there evidence of the existence of complex ions.

This investigation is being extended to a study of the products of the atmospheric oxidation of alcoholic solutions of cobalt salts in the presence of various other amines.

The authors wish to express their grateful thanks to the Depa
ment of Scientific and Industrial Research for the award of
research grant to one of them (W. R. B.), and to the Chemic
Society for a grant in aid of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, June 9th*, 1928.]

CCCXLIX.—*The Density of Boric Oxide Glass an the Atomic Weight of Boron.*

By ARNOLD COUSEN and WILLIAM ERNEST STEPHEN TURNER.

IN an important paper on this subject, Briscoe, Robinson, ar Stephenson (J., 1926, 70) were concerned, not with the absolu atomic weight of boron, but with the relative values for the elemei present in boron minerals obtained from various terrestrial source and in the discussion of the results they were inclined to think tha the maintenance by them of the same conditions of preparation c the boric oxide glass samples would ensure a valid comparison c density values even supposing some slight error might be present i the absolute values due to the inclusion of minute traces of moisture

Of the six preparations of boric oxide, obtained from differen sources, the densities ranged between 1·79711 (at 17·36°) an 1·79404 (at 19·25°), corresponding to extreme variations in cal culated atomic weights for boron of 10·847 and 10·788. Thes differences in densities are substantial, being no less than three unit in the third place of decimals. Differences in the temperature o determination in no way account for them: as the authors them selves indicate, a temperature change of 0·1° should only modify th density by one unit in the eighth decimal place. Consequently, th authors were led, in conjunction with certain other evidence, t conclude "that boron, like lead, has an atomic weight varying witl its source."

In reopening this subject for discussion, we have no observation to make on the evidence previously obtained by Briscoe an Robinson (J., 1925, **127**, 696) on the basis of their determination o the ratio BCl_3 : Ag, but we are concerned with the density deter minations on boric oxide glass and with their interpretation; fo when reading the paper of Briscoe, Robinson, and Stephenson on it publication, doubt immediately occurred to one of us of the adequacy of the tests for strain in the beads of fused boric oxide. The author stated: "A number of test beads examined . . . between crossed Nicols, appeared free from strain." It is by no means easy, however

o detect in such a way strain existing in small spherical objects, and the authors might well have been misled. Moreover, the magnitude *of the change brought about in the numerical values of physical* properties of glasses due to the existence of stresses is not fully realised except by workers on the vitreous state. Pure boric oxide glass and glasses containing boric oxide are particularly susceptible to modification of physical properties according to the rate at which the specimens have been cooled.

Whilst the rapid chilling which the beads of fused boric oxide underwent as the result of dropping small quantities of the molten material into a cold platinum basin made us feel considerable doubt about the beads being strain-free, the very fair concordance between the results for the samples prepared from six different sources at first disarmed criticism. At the time of publication we were engaged in the study of the vitreous system boric oxide–silica, and later we directed our attention to the densities of preparations in this system. Our first determinations on samples prepared from slightly impure boric oxide gave $d_{4^\circ}^{25^\circ}$ 1·843, a value much higher than those of Briscoe, Robinson, and Stephenson. It seemed desirahle, therefore, that we should investigate carefully this discrepancy. The account which follows is a hrief summary of the work undertaken, the stages enumerated below, however, not necessarily appearing in the sequence in which they were investigated. The several factors considered as possible to account for the discrepancy were five in number.

1. *The Influence of Purity of the Sample.*—The boric acid utilised by us as the source of boric oxide in the earlier experiments was B.P. material containing total impurity of only 0·17%, equivalent to approximately 0·31% in the horic oxide prepared from it by fusion at 1400°. The densities obtained for a well-annealed horic oxide glass from material of the purity stated lay between 1·843 and 1·845 in various determinations.

The same boric acid when recrystallised once from 10% hydrochloric acid and three times from distilled water was found by repeated evaporation with pure methyl alcohol to contain impurity not exceeding 0·02%. The density of eight samples of well-annealed boric oxide glass prepared from this purified acid lay between 1·8435 and 1·8446.

2. *The Influence of the Method.*—Our earlier determinations were carried out by the displacement method, a specific gravity bottle being used, and hy critical tests we were satisfied that the densities obtained by means of it were trustworthy to within 0·1%, a trifling error compared with the discrepancy between our values and those of Briscoe, Robinson, and Stephenson. To ensure still greater accuracy in the later stages of the investigation, we used a flotation

method with pentachloroethane and trimethylene dibromid liquids which had been found suitable by the above authors. Th mean of four determinations on well-annealed boric oxide samples i the case of the specific gravity bottle method was 1·8444, and fro the flotation method 1·8439.

3. *The Influence of a Trace of Moisture and of the Temperature Preparation.*—Fused boric oxide is hygroscopic and readily absorb moisture on its surface, becoming opalescent in the process. A brigh bead of boric oxide was balanced in the flotation liquid and the exposed to the atmosphere for 90 minutes; after exposure, it floate on the surface, indicating a diminution in density due to absorp tion of moisture, which was also indicated visually by a distin opalescent film.

Experience over several years in the preparation of fused bor oxide glass has indicated that the last traces of water are eliminate with difficulty on fusing boric acid, and a temperature of 900° insufficient. It appeared to us quite possible that the temperatu employed by Briscoe, Robinson, and Stephenson may not have bee adequate, for their fusion was carried out in a covered platinu crucible for 4—5 hours at 900°, followed by heating over a Mék burner and a final heating in a Bunsen flame of beads gathered fro the crucible by a loop of platinum wire, and it is probable that th maximum temperature attained cannot have exceeded 1000°. Ou own samples were prepared by fusion in platinum at 1400°; but i order to test the effect of temperature, a few beads were prepared b fusing boric acid at 1000° for 4 hours and subsequently followin the procedure of Briscoe, Robinson, and Stephenson. The lowe density values obtained by us in our series of measurements we with the beads prepared at 1000° [see (5) on p. 2657], and it seem quite likely, therefore, that a small amount of moisture is sti retained even after fusion at that temperature.

4. *The Effect of Annealing.*—This factor proved, without doubt, t be the cause of the big discrepancy between our results and those Briscoe, Robinson, and Stephenson. We had already made measure ments of the thermal expansion of fused boric oxide over the whol range of temperature up to the softening point, and had, therefor been able to deduce the cooling curve requisite for thorough annealin In a series of measurements on unannealed specimens, obtained b dropping beads into a cold platinum dish, the densities were found t lie between 1·8008 and 1·8067.

The care which must be exercised in annealing glasses require for precise physical measurements is illustrated in the followin table, which contains the data for several sets of specimens, one grou of them having been cooled more rapidly than the other.

1. *Rate of Annealing.*

Temp.	345°	325°	300°	275°	240°	205°	160°
Time (hours), Curve I ...	0·5	1·5	2·5	3·5	4·5	5·5	6·5
,, ,, ,, II ...	0·5	2·5	4·5	6·5	8·5	10·5	12·5

2. *Densities by Flotation Method.*

Sample No.	Size of bead (mm.).	Rate of annealing.	Density.
5*a*	3·2 × 4·7 × 5·8	As Curve I	1·8423
5*b*	3·3 × 4·5 × 7·0	,, ,,	1·8423
6*a*	—	,, ,,	1·8418
6*b*	—	,, ,,	1·8414
7*a*	(2·2 × 2·8) (two beads) (2·1 × 2·7)	As Curve II	1·8442
7*b*	(3·2 × 5·3) (two beads) (4·7 × 9·8)	,, ,,	1·8437
8*a*	—	,, ,,	1·8440
8*b*	—	,, ,,	1·8435

When the beads were cooled between 345° and 160° during the comparatively long time of 6½ hours, the densities were still some 2 units in the third place lower than when 12½ hours were devoted to cooling over the same range.

5. *The Influence of Bead Size.*—This question of size is bound up with the question of rate of cooling. In experiments with the boric oxide prepared at about 1000°, the beads being unannealed, a density of 1·8017 was obtained for a bead weighing 0·070 g. and 1·7929 for a bead of 0·111 g.

The results of this investigation indicate, in the first place, that the true density of pure fused boric oxide glass at a temperature between 18° and 25° is not 1·7952, as stated by Briscoe, Robinson, and Stephenson, but is more accurately 1·844 (the mean value of the results by the specific gravity bottle method being 1·8444, and by the flotation method 1·8439). Further, the low figures obtained by these authors are mainly due to inadequate annealing of the specimens, and, probably in a minor degree, to the fusion of the boric oxide at about 1000° only. It is clear from results obtained in this Department that in themselves the variations obtained by these investigators in the density results of boric oxide glass from six different terrestrial sources cannot be used as evidence in favour of the view that the atomic weight of boron varies according to the source of the mineral which contains it.

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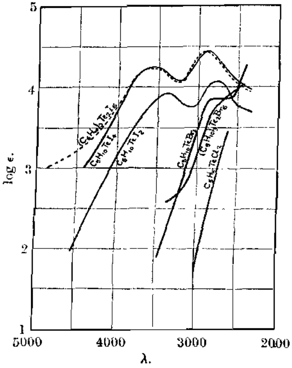
CCCL.—*Studies in Valency. Part XI. Molecul Conductivities and Extinction Coefficients of Deri atives of* cyclo*Telluropentane.*

By Frank Lathe Gilbert and Thomas Martin Lowry.

Through the kindness of Professor G. T. Morgan and Dr. I Burgess, we have been able to extend our investigation of tl dimethyltelluronium salts (this vol., pp. 307, 1997) by measurir the molecular extinction coefficients in dry alcohol, and the molecul conductivities in water, of the compounds of *cyclo*telluropentar

Fig. 1.

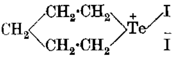
Molecular extinction coefficients of cyclic tellurium compounds.

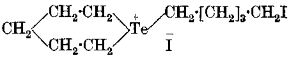


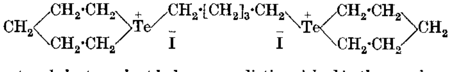
recently described by them (*ibid.*, p. 321). In addition to examining the dihalides of the three series, represented by (I), (II), and (III), we have prepared and examined the base $C_5H_{10}TeO$ or $C_5H_{10}Te(OH)_2$, the hydroxy-halides $C_5H_{10}Te(OH)X$, and the *tetraiodide* $C_5H_{10}TeI_4$, of the monocyclic series, and the base $(C_5H_{10})_3Te_2(OH)_2$ of the dicyclic series, as well as the histribromide and the *bistri-iodide* of the latter series. In the case of the bases, the measurements included a potentiometric titration.

Absorption Spectra.—The molecular extinction coefficients are plotted in Fig. I and the most important values are summarised in Table I. Most of the observations followed the course that we

should have anticipated on the assumption that the dihalides may be represented by formulæ such as (I), (II), and (III), where the


(I.)


(II.)

(III.) 

covalent and electrovalent halogen are distinguished in the usual way. Thus the cyclic dichloride gave only a general absorption, as in the case of the two dimethyl compounds. The cyclic dibromide, however, gave a step-out, log $\varepsilon = 3{\cdot}85$ at λ 2600—2850, just as in the case of the α- and β-dimethyl compounds, which gave a similar step-out, log $\varepsilon = 3{\cdot}7$ and $4{\cdot}0$, respectively, at λ 2600—2800. At longer wave-lengths, however, the absorption of the cyclic dibromide agrees closely with that of the α-dibromide, and is very much less than that of the β-dibromide, which is sufficiently strong in the visible region to give the compound a bright yellow colour, which is lacking both in the isomeric α-compound and in the cyclic dibromide.

The monocyclic di-iodide (I) separates from hot or cold benzene in a purple form, but the surface becomes yellow if the solution is allowed to dry on the crystals. When the purple form is heated, it begins to pass into the orange form at about 90° and changes rapidly at 110°; the purple form also becomes orange in boiling water before it dissolves. The transition temperature is therefore below 100°, but is not easy to determine precisely on account of the lag in the transformation, even with rising temperatures. The reverse change from orange to purple takes place in a few minutes at the ordinary temperature, but is slower if the orange form has been kept for some time above 100°. The clear orange crystals which are obtained when the di-iodide separates from hot carbon tetrachloride may persist for some weeks at atmospheric temperature before becoming purple, even when exposed to air and light; and a crystal which exhibits both colours may persist for some days before it changes completely into the purple form.

A careful comparison showed that the absorption spectra of the two forms in cold alcoholic solutions are identical within the limits of experimental error. The spectrum shows the twin maxima of the "iodoform band," the maximum extinction coefficients being log $\varepsilon = 3{\cdot}9$ at 3380 and log $\varepsilon = 4{\cdot}05$ at 2770. The intensities of two maxima are similar to those of the dimethyl di-iodides (of which

the α-compound gave log ε = 3·7 and 4·05, whilst the β-compound gave log ε = 3·8 and 4·25), but in the visible region the absorption of the cyclic di-iodide again corresponds with that of the α-dimethyl di-iodide, since the curve falls away steeply from the maximum, instead of showing the wide extension of the foot of the band which accounts for the deeper colour of the β-di-iodide.

The cyclic di-iodide (I) also resembles the α-dimethyl di-iodide, and differs from the β-di-iodide in that it readily forms a tetraiodide $[C_5H_{10}TeI]^+I_3^-$. This compound, which we prepared by mixing equimolecular solutions of the di-iodide and of iodine in chloroform, and boiling the mixture under reflux for 10 minutes, separated as a black solid, and crystallised from methyl alcohol in shining, black crystals. It melts at 82—84° to a black oil, which is slowly dissolved (like the di-iodide) by boiling water, but to a very limited extent. Its absorption spectrum is similar to that of the di-iodide, but of practically twice the intensity throughout, since both ions of the salt give rise to twin maxima at nearly the same wave-length and intensity (log ε = 4·28 and 4·45, obs.; 4·25 and 4·43, calc.).

According to the views expressed in our previous paper, *both* atoms of halogen in the dihalides of type (III) should be ionised in the same way as in the trimethyltelluronium halides. This conclusion is confirmed by the fact that the di-iodide $(C_5H_{10})_3Te_2I_2$ is readily converted into a black hexaiodide, $(C_5H_{10})_3Te_2I_6$. This compound, which we prepared by mixing the cyclic di-iodide with 2 mols. of iodine in chloroform, and boiling the mixture under reflux for 10 minutes, separated as a black solid melting at 127—129°, but could not be recrystallised on account of its sparing solubility. In order to observe its absorption spectrum, 0·0125 g. was dissolved in 10 c.c. of dry methyl alcohol, and the solution examined at *M*/5000. The spectrum showed the twin maxima of the tri-iodide ion, with the same two-fold intensity as in the monocyclic tetraiodide (log ε = 4·25 and 4·44, obs.; 4·30 and 4·50, calc.), but with a wider " foot " in the visible region of the spectrum, to correspond with the greater absorption in this region of the tri-iodide ions. The hexabromide, described by Morgan, was also examined in methyl alcohol, and gave a general absorption with clear indications of a maximum, log ε >4, just beyond λ 2400, and the beginnings of a step-out, which could not be traced to longer wave-lengths than 3400 on account of the limited solubility of the product (the tribromide ion in $C_6H_4Br\cdot\overset{+}{N}Me_3\overset{-}{Br_3}$ gives a maximum, log ε = 3·4 at λ 2600, and a step-out, log ε = 1·8 at λ 3900).

The remaining compounds of series (II) and (III) gave only a general absorption of light, in agreement with the conclusion that

TABLE I.

Extinction Coefficients in Alcohol of Halogen Derivatives of cyclo-*Telluropentane.*

(*a*) Selective absorption.

		λ.	log ε.	λ.	log ε.
$C_5H_{10}TeI_2$	Maxima at	3380	3·92	2770	4·05
$C_5H_{10}TeI_4$	,, ,,	3560	4·28	2880	4·45
$(C_5H_{10})_3Te_2I_6$ (in MeOH)	,, ,,	3560	4·26	2900	4·44
$C_5H_{10}TeBr_2$	Step-out at λ = 2600 to 2850.			log ε = 3·85.	

(*b*) General absorption.

	Wave-lengths for integral values of log ε.					
	log ε = 1·5.	2·0.	2·5.	3·0.	3·5.	4·0.
$C_5H_{10}TeCl_2$		2950	2840	2730		
$C_5H_{10}Te(OH)I$ (in water)		2870	2690	2480		
$(C_5H_{10})_2TeI_2$	3460	3130	2980	2750		
$(C_5H_{10})_2TeBr_2$		2800	2500	2340		
$(C_5H_{10})_2TeCl_2$	2680	2520	2340			
$(C_5H_{10})_3Te_2Br_2$		2900	2580	2420		
$(C_5H_{10})_3Te_2I_2$				2830	2330	
$(C_5H_{10})_3Te_2Br_6$ (in MeOH)				3070	2920	2500

none of the halogen is joined to the metal by a covalent bond. The rather heavy general absorption of the iodide (II) can be explained by the presence of the group $-CH_2I$, but this explanation is not available in the case of the iodide (III).

Molecular Conductivities.—The methods used have already been described (this vol., p. 308), but attention may be directed to the fact that a few sparingly soluble compounds, which it was undesirable to hydrolyse by boiling with water, were dissolved in a minimum quantity of alcohol and diluted with not less than 20 volumes of conductivity water. The validity of the corrections applied to these solutions has already been demonstrated in the case of α-dimethyltelluronium di-iodide (this vol., p. 313).

The molecular conductivities shown in Table II are for the most part in agreement with the values which we should have predicted from the preceding formulæ, with the help of the data already obtained for the dimethyl compounds. Thus, the dihalides of type (II) behave as *binary* electrolytes, like the hydroxy-halides of the dimethyl series, or the simple halides of the trimethyl series, and give values of $\Lambda^{25^\circ} =$ *ca.* 100. In the same way, the dihalides of type (III) behave as *ternary* electrolytes, giving $\Lambda^{25^\circ} =$ *ca.* 200. The dihalides of type (I), however, gave the same anomalous values, $\Lambda^{25^\circ} =$ *ca.* 500, which were observed previously in the dimethyl series, so that once more it was clear that, whereas one halogen is *ionised* more or less completely, the other is *hydrolysed* to a similar degree. The tetraiodide of type (I) gave similar values, $\Lambda^{25^\circ} =$ *ca.* 500, and was evidently hydrolysed according to the scheme

$$[C_5H_{10}TeI]I_3 + H_2O \rightleftharpoons [C_5H_{10}TeOH]I_3 + HI.$$

An unexpected result was obtained, however, when the bis-tri-bromide of type (III) and the analogous bis-tri-iodide were dissolved in boiling water and cooled to 25°, since, instead of behaving as ternary electrolytes, with $\Lambda^{25°} = ca. 200$, their solutions gave molecular conductivities of the order $\Lambda^{25°} = 1000$. This anomaly can be explained most readily by supposing that the compounds are decomposed according to the scheme

$$C_5H_{10}{:}TeI_3{\cdot}C_5H_{10}{\cdot}TeI_3{:}C_5H_{10} \longrightarrow 2C_5H_{10}{:}TeI_2 + C_5H_{10}I_2$$
$$\longrightarrow 2[C_5H_{10}{:}TeOH]I + 2HI + C_5H_{10}I_2$$

The conclusion that the high conductivities of this compound are due to a progressive decomposition was established by dissolving the polyiodide in cold alcohol and diluting it with cold water, whereupon we found $\Lambda^{25°} = 106$, reckoned on the total concentration of the polyiodide, part of which, however, was still undissolved. When the solution was warmed, the value rose to $\Lambda = 136$ at 40°, and $\Lambda = 315$ at 100°. Finally, after some minutes' boiling, when all the material had dissolved, the conductivity rose to $\Lambda^{25°} = 794$, or $\Lambda^{25°} = 930$ when corrected for the alcohol used as solvent, in good general agreement with the values recorded in Table I.

The hydroxy-halides, which are formed by the hydrolysis of the monocyclic dihalides, were prepared by mixing the free base (see below) and the dihalides in molecular proportions, and were found to behave as strong binary electrolytes, just as in the case of the hydroxy-halides prepared from Vernon's salts. The conductivities agree more nearly with those of the α-series than of the β-series, but we cannot lay any stress on this fact, as we have not yet found a satisfactory explanation of the higher values recorded for the latter compounds. In the case of the free bases, however, where there is a much greater contrast between the α- and β-series, the conductivities of the cyclic compound are much lower than those of Vernon's β-base, and differ only to an insignificant extent from the very small values already recorded for the α-base at similar dilutions.

Potentiometric Titration of the Bases.—(*a*) The *monocyclic base*, $C_5H_{10}Te(OH)_2$ or $C_5H_{10}TeO$, was prepared by grinding the dibromide with freshly prepared silver oxide; when the solution was evaporated to dryness in a vacuum, the base was obtained as a colourless solid, but the quantity was not sufficient for an analysis to show whether the base was anhydrous or hydrated. On re-dissolving, it gave the same reactions as the original base with acids, with silver nitrate, and with ferric chloride, and hence was not converted into an isomeride under the conditions which cause Vernon's α-base to change into the β-base. With hydriodic acid, the base gives a

TABLE II.

Molecular Conductivities Λ^{25° *of Derivatives of* cyclo*Telluropentane.*

	v = 128.	256.	512.	1024.	2048.	4096.
Type I.						
$C_5H_{10}TeCl_2$		475	482	491	482	478
$C_5H_{10}TeBr_2$		481	485	493	492	489
$C_5H_{10}TeI_2$ (orange)			476	484	484	469
$C_5H_{10}TeI_2$ (purple)			473	486	493	478
$C_5H_{10}TeI_2$ (purple) 5% alcohol at $v = 512$ (corrected values).			474	479	483	474
$C_5H_{10}TeI_4$ 4·5% alcohol at $v = 1024$ (corrected values).				488	491	493
$C_5H_{10}Te(OH)Cl$	96	98	102	105	107	112
$C_5H_{10}Te(OH)Br$	96	100	104	108	110	112
$C_5H_{10}Te(OH)I$		97	102	107	110	111
$C_5H_{10}Te(OH)_2$	5·5*	6·4	8·0	10·6		
Type II.						
$(C_5H_{10})_2TeCl_2$		92·5	94·4	96·5	98	101
$(C_5H_{10})_2TeBr_2$		90·5	94·4	96·5	99	102
$(C_5H_{10})_2TeI_2$		92	96	98	101·5	104
Type III.						
$(C_5H_{10})_3Te_2Br_2$		199	209	219	225	232
$(C_5H_{10})_3Te_2I_2$		185	197	206	213	219
$(C_5H_{10})_3Te_2Br_6$			1074	1098	1115	1114
$(C_5H_{10})_3Te_2I_6$					965†	986‡

* At $v = 42·6$, $\Lambda^{25^\circ} = 4·2$, and at $v = 64$, $\Lambda^{25^\circ} = 4·6$.
† For $v = 2260$. ‡ For $v = 4520$.

canary-yellow precipitate, m. p. 136—137°, which is probably the orange form of the cyclic di-iodide, m. p. 135—136°. This precipitate does not change colour when heated to its m. p., but turns purple (or dark red) when compressed with a spatula, and retains this colour when the pressure is released. The dark red form reverts *to the yellow form at 115°*, but this *does not change* back to red on cooling.

A potentiometric titration was made, with a glass electrode, of an $N/45$-solution, which was neutralised with N-hydrochloric acid. The resulting curve is plotted in Fig. 2. The free base gave $p_H = 8·3$, in close agreement with the value for the α-dimethyl base. The equivalence point was $p_H = 4·1$, the values at 98% and 102% neutralisation being 5·1 and 3·4, a range of 1·7 units. At half-neutralisation $p_H = 6·8$, whence $-\log K_B = 7·2$ and $K_B = 6·3 \times 10^{-8}$. The titration curve almost coincides with that of Vernon's α-base; but it differs fundamentally from the curve for the β-base, in that it shows no sign of an intermediate inflexion.

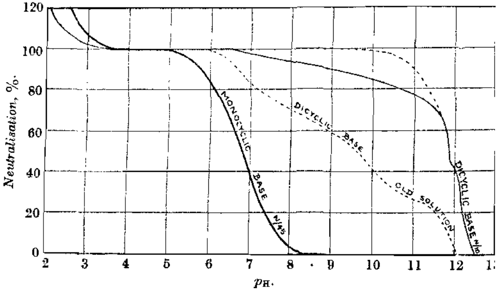
(*b*) The *dicyclic base*, $(C_5H_{10})_3Te_2(OH)_2$, was prepared by the action of silver oxide on the di-iodide or dibromide. In order to

obtain a good yield, it was necessary to grind the di-iodide witl silver oxide for 2—3 hours, whereas ½ hour is ample for the con version of the monocyclic di-iodide and the dimethyl di-iodide into the corresponding bases. A quantitative experiment with weighed quantity of the dicyclic di-iodide showed that under thes conditions the neutral point with methyl-orange corresponds closel with that calculated for neutralisation of both hydroxyl groups o the base. After evaporation and dissolution, the base gave the sam reactions as before towards silver nitrate, picric acid, hydriodic acid and ferric chloride.

A curve for the potentiometric titration of an $N/10$-solution c the dicyclic base with a glass electrode against N-hydrochloric aci

FIG. 2.

Potentiometric titrations.



is shown in Fig. 2. The solution was freshly prepared, since les than 1 hour elapsed between the preparation of the base and th commencement of the titration. The dicyclic compound is a stron base, which gave $p_H = 12{\cdot}5$ at $N/10$ or $M/20$, in marked contras with the weak monocyclic base, which gave $p_H = 8{\cdot}3$ at $N/45$. A slight break, corresponding to the neutralisation of the first hydroxy group, was observed at 50% neutralisation, but this could easily hav been obliterated in drawing the diagram. At about 75% neutralis ation the readings became unstable and began to drift towards th alkaline side, the largest drift being about 44 millivolts or 0·8 in th value of p_H. The values plotted in Fig. 2 were obtained after a interval of about 15 minutes, when the drift had become very slow but we cannot be sure that they were the final equilibrium values and it is possible that after long delay the values might have drifted

to those required to give the typical (broken) curve for a strong base. At 80—100% neutralisation the drift was more rapid, and at 100% steady values were obtained immediately.

The abnormalities described above were confirmed in almost every detail by a duplicate determination with a freshly prepared $N/14{\cdot}5$ (or $M/29$)-solution. A third solution, of concentration $N/14$, which had been made up for about 9 days, however, gave a more abnormal curve, which straggled across from an initial value $p_H = 12$, to $p_H = 6$ at 100% neutralisation. Similar abnormalities were observed in the conductivities of these solutions. Thus the equivalent conductivities of the solution which was used for the first potentiometric titration, when examined 2 days after it had been prepared, had the following values at 20° :

v	71·5	143	286	572	1144
$\Lambda^{20°}$	190	195	197	197	196

Since the mobility of the bivalent kation $(C_5H_{10})_3Te_2^{++}$ is about 34×2, whilst that of the hydroxyl ion at 20° is about 178, these are normal values for a strong base with $\Lambda^{20°}_{\infty} = ca.\ 210$. On the other hand, the third solution, when 10 days old, gave the following equivalent conductivities at 25° :

v	100	200	400	800	1600
$\Lambda^{25°}$	116	122	126	129	129

These conductivities are about one-third less than those recorded for the first solution, whereas they should be about 8 units higher to allow for a temperature difference of 5°.

Although we cannot offer any precise explanation of these anomalies, they are clearly due to a locking-up of the basic properties of the hydroxide by a reversible process which may be compared with the formation of a pseudo-base. This view is supported by the fact that a progressive decrease of conductivity was observed in a freshly prepared solution of the base, which gave the following readings (R = resistance ; t = time, in hours) :

t ...	0	0·5	1	2·8	4·5	6	22	46	95	101	119	142
R ...	88·5	90·1	90·8	90·9	91·1	91·3	93·8	96·8	101·5	102	103·5	105
$\Lambda^{25°}_{59}$	142										121·5	119·5

In this case, the conductivity fell progressively from an initial value, which was approximately mid-way between those of the first and third solutions, to a final value, which was approximately the same as the latter. The strength of the solution, as tested by titration with methyl-orange as indicator, however, was exactly the same at the end of 6 days as when tested initially. On the other hand, another freshly prepared solution had already reached a steady value $\Lambda^{25°}_{47} = 117$ at the end of 5 minutes from the time when the

base was extracted from the silver oxide, and maintained it with small fluctuations during a period of 2 days:

t	0·1	0·4	2·5	4	5·5	21·5	30	46	48
R	86·0	86·0	85·4	85·0	85·6	85·2	87·5	87·0	87·0

These observations show that solutions of the dicyclic base are subject to wide variations of properties, depending on the age of the solutions and on other factors which are still obscure; but no more material was available to enable us to pursue the enquiry any further.

Action of Alkalis on the Cyclic Di-iodide.—The most striking contrast between Vernon's α- and β-compounds is found in the fact that the α-di-iodide yields sparingly soluble basic iodides when acted on by alkalis, whilst the β-di-iodide undergoes a molecular rearrangement, which can be compared with a pinacol–pinacolin transformation, since it gives rise to trimethyltelluronium iodide as one of the products. In order to find out which type of behaviour is characteristic of the monocyclic iodides, the purple di-iodide was boiled with a concentrated aqueous solution of potassium carbonate, and evaporated to a small bulk. The colourless crystals which separated decomposed at 195° and contained 39—41% I, whereas the monoxyiodide $(C_5H_{10})_2Te_2OI_2$ would require 38·3% I. The compound resembled Vernon's α-monoxyiodide in being soluble in water and neutral to methyl-orange, but differed from it in that it did not change colour in air.

A colourless solid obtained by grinding the solid di-iodide with concentrated aqueous ammonia turned yellow on exposure to the air or when heated at 100°; it contained 34% of iodine, gave a neutral aqueous solution, and blackened and decomposed at 150°.

The products obtained by the action of potassium carbonate and of ammonia on the monocyclic di-iodide are obviously quite distinct from the dicyclic di-iodide, $(C_5H_{10})_3Te_2I_2$, which would be the analogue of the trimethyltelluronium iodide formed in Vernon's transformation of the β-salt; on the other hand, their composition and properties are those of basic iodides, and therefore confirm the conclusion that in this respect also the cyclic di-iodide exhibits the behaviour of an α- rather than of a β-salt.

Summary.

Measurements have been made of the molecular conductivities and extinction coefficients of the cyclic tellurium compounds recently described by Morgan and Burgess. The tertiary salts behave as strong electrolytes, like $TeMe_3I$, but the secondary salts resemble $TeMe_2I_2$ in losing one molecule of halogen by hydrolysis,

giving rise to hydroxy-halides. Observations of the conductivities of the base and of the form of the curve obtained from a potentiometric titration, together with the absorption spectrum of the iodide and its behaviour towards iodine and towards alkalis, show that the cyclic compounds resemble Vernon's α- (or *trans-*) series of compounds rather than the isomeric β- (or *cis-*) compounds.

We are indebted to Professor Morgan and Dr. Burgess for specimens of the cyclic tellurium compounds, and to the Department of Scientific and Industrial Research for a maintenance grant to one of us (F. L. G.) during the period within which the research now described was carried out.

Chemical Laboratory,
University of Cambridge. [*Received, June 7th*, 1928.]

CCCLI.—*An Investigation on the Ceria–Thoria Catalysts.*

By A. B. Goggs.

It has been shown by Swan (J., 1924, **125**, 780) that, of all the mixtures of ceria and thoria, that used in the gas mantle (CeO_2 1%; ThO_2 99%) is the most efficient for bringing about the oxidation of hydrogen. The present investigation was undertaken to determine whether this mixture was also the most efficient for the combustion of other gases, the gas chosen being carbon monoxide.

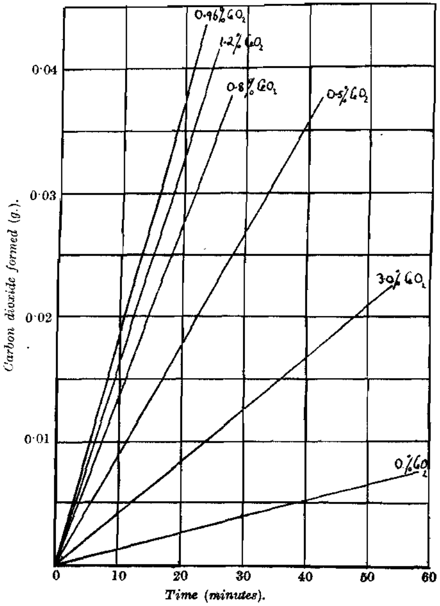
Thorium nitrate was purified by the method of Neish (*J. Amer. Chem. Soc.*, 1904, **26**, 781), the details being essentially the same as those used by Swan (*loc. cit.*). Cerium ammonium nitrate was prepared by the method of Imry (*Z. anorg. Chem.*, 1927, **164**, 781) and recrystallised three times from 10·5*N*-nitric acid. Carbon monoxide, prepared from redistilled formic acid and pure sulphuric acid, was mixed with pure oxygen, prepared from potassium permanganate, in the proportion of 2 : 1 by vol.

The solutions of the nitrates were mixed in the requisite proportions and the mixed oxalates were precipitated with recrystallised oxalic acid and boiled with a slight excess of oxalic acid to reduce the ceric salt to the cerous state, the same quantity of oxalic acid being used in each case. The precipitates were filtered off, and ignited to constant weight at as low a temperature as possible; they were then sieved, made into a paste with water, spread evenly on thin glass slips (2·2 × 0·4 mm.), and dried at 140° for 5 hours.

Experiments were at first conducted in an apparatus similar to Swan's (*loc. cit.*), but unsatisfactory results were obtained on account

of the accumulation of the carbon dioxide over the catalyst and t impossibility of starting to take readings at corresponding tim The following experiments were made by passing the carb monoxide-oxygen mixture (freed from carbon dioxide) at consta

FIG. 1.



pressure through a flow-meter over the catalyst in a hard-glass tub in the furnace, collecting the carbon dioxide formed in two flask containing barium hydroxide of known strength, and titrating th excess of barium hydroxide, phenolphthalein being used as indicator Care was taken that the catalyst was always in the same part of th tube so that the pre-heating of the gases should be the same in all

cases. The glass slip was put flat on the bottom of the tube. The temperature employed was 485°.

The following were the results obtained, each experiment being made with a different catalyst-slip. It is seen that the rate of formation of carbon dioxide (dc/dT) attains a maximum at 0·96% of ceria (see also Fig. 1), and hence that the catalyst which Swan had found to be most efficient in the oxidation of hydrogen is also the most efficient for that of carbon monoxide.

Catalyst, $\%CeO_2$.	Time, mins.	CO_2 formed, g.	$10^4 \times dc/dT$.	Mean.
0	60	0·0079	1·317	
	60	0·0077	1·283	1·30
	60	0·0079	1·317	
0·5	40	0·0362	9·05	
	30	0·02745	9·15	9·0
	30	0·0265	8·83	
0·8	30	0·0410	13·67	
	30	0·0436	14·53	14·0
	30	0·0415	13·83	
0·96	15	0·0270	18·0	
	15	0·0268	17·85	18·0
	15	0·0274	18·25	
1·2	15	0·0240	16·00	
	15	0·0245	16·35	16·2
3·0	60	0·0287	4·78	
	30	0·0121	4·02	
	30	0·0131	4·37	4·3
	30	0·0125	4·17	

My thanks are due to Professor Baker for his encouragement and help during this investigation.

ROYAL COLLEGE OF SCIENCE,
LONDON, S.W.7. [*Received, July 19th*, 1928.]

CCCLII.—*Studies in the Composition of Coal. Oil-yielding Constituents.*

By RONALD HOLROYD and RICHARD VERNON WHEELER.

BITUMINOUS coal being a conglomerate of different types of compounds which decompose at different temperatures, yielding characteristic liquid and gaseous products, it is reasonable to suppose that by the slow destructive distillation of the coal as a whole the contributions of each type of compound to the distillates might be recognised. In particular, it would seem probable that those constituents of the coal which, when separated therefrom by means of solvents, are found to melt below 100° (see Cockram and Wheeler, J., 1927, 700) should become liquid and flow from the coal at quite low temperatures. The work of Burgess and Wheeler (J., 1914,

105, 131) and, more recently, of King and Willgress (Fuel Research Board Tech. Paper No. 16, 1927) is significant in this connexion.

We have carried out slow destructive distillations, in a vacuum, of a number of bituminous coals, using varieties which had already been studied by solvent analysis and other means, so that their general character was known. We record in detail in this paper the results obtained with one coal, bright coal (mixed vitrain and clarain) from the Wigan Six Foot seam.

The main conclusions to be drawn from the results (which experiments with other coals amply confirm) are: (1) That the hydrocarbons and resins, extractable from the coal by organic solvents, yield a high proportion of the oils obtained on distillation, the former being distilled unchanged, quantitatively, and the latter partly distilled and partly decomposed. (2) That the coal has a definite decomposition point, which is not appreciably affected by changes in the experimental conditions. With the Wigan Six Foot coal the decomposition point occurs at 318°. Characteristic products of this decomposition, which is of the ulmin constituents of the coal, are water and phenolic compounds. As soon as the decomposition point of the coal has been passed, its character, as evinced by its behaviour towards solvents, its caking-power, and its reactivity in general, undergoes a sudden and marked change.

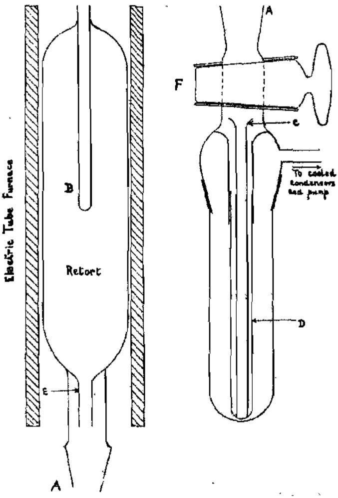
EXPERIMENTAL.

The method of experiment was similar to that used by Burgess and Wheeler (*loc. cit.*). A charge of 250 g. of the undried coal, ground to pass a 20-mesh and remain on a 50-mesh sieve (I.M.M. standard), filled a cylindrical retort of Jena glass, fixed vertically with its mouth downwards. The retort (see Fig. 1), which was heated electrically in a tube furnace specially designed to secure a uniform temperature throughout its length, was connected by a ground glass joint, A, through a series of three condensers, to an automatic mercury Sprengel pump. A glass tube, B, reaching to the centre of the charge of coal, was fused into the head of the retort for the reception of a thermo-couple. A second thermo-couple was lashed to the outer wall of the retort. The required temperature was regulated by means of the outside thermo-couple. About 12 hours elapsed before the inside thermo-couple recorded the same temperature as the outside, but thereafter both records remained constant and identical.

A difficulty encountered with regard to the collection of the less fluid oils distilled from the coal, which it was desired to separate at intermediate stages of the heating, arose through their condensation at the neck of the retort, whence they could be removed only after

dismantling the apparatus. To obviate this difficulty, the arrangement shown in Fig. 1 was devised. A glass tube, C, bearing a small cylinder of soft iron at its lower end, was placed within a test-tube, D, and the two were inserted within the first of the series of three condensers connected to the retort. When the apparatus was assembled for an experiment, the whole being thoroughly evacuated, the tube C was raised by means of a solenoid, so that its upper end fitted closely over the mouth of the retort at E. It was then gripped in position by slightly turning the wide-bore tap, F. At any stage in the distillation of the coal the tube C could be withdrawn below the tap F (which could then be closed) and the oils that had condensed within it examined.

FIG. 1.



Method of Carrying out a Distillation.—After evacuation of the apparatus, the temperature of the charge of coal was slowly raised to 100° and maintained continuously during 120 hours. Any liquid and gaseous products evolved were collected, the former in the condensers, the second and third of which were cooled by immersion in solid carbon dioxide dissolved in ethyl ether, and the latter over mercury at the Sprengel pump. The temperature was now raised over the second desired range, 48 hours being taken in doing so, and maintained at the higher value during 120 hours, the liquids and gases evolved being collected as before. And so for each temperature range. The pressure within the apparatus, even at periods of maximum gas-evolution, never exceeded 3 and was usually less than 1 mm.

Examination of Liquid Products.—The liquid products were collected in two portions over each temperature range: (1) Water

and "light oils" condensing at $-80°$ in the two cooled receivers and (2) "heavy oils" condensing at atmospheric temperature i the first receiver. The "light oils," consisting mainly of ligh petroleum, were weighed but not closely examined. The "heav oils" were analysed in the following manner. A chloroform solu tion of them was washed successively with dilute solutions of sodiun carbonate, potassium hydroxide, and sulphuric acid, from whicl solutions acidic, phenolic, and basic oil fractions were recovered The residual neutral oil was extracted in a Soxhlet apparatus suc cessively with light petroleum, ethyl ether, and chloroform. Th extract by light petroleum, consisting mainly of hydrocarbons, wa treated with concentrated sulphuric acid, thereby making a separation of saturated from unsaturated compounds, and in some experiments the saturated compounds were treated with fuming sulphuric acid and nitration mixtures for the removal of aromatic compounds.

Distillation of Wigan Six Foot Coal.—The sample of coal used for these experiments was the bright portion of the seam, a clarain with numerous streaks of vitrain. It contained 2·7% of ash and the ultimate analysis, on the ash-free dry coal, was: C, 81·8; H, 5·5; O, 9·24; N, 1·52; S, 1·94. Solvent analysis (see Cockram and Wheeler, *loc. cit.*) by pyridine and chloroform gave: Insoluble in pyridine (α), 81·54; soluble in pyridine but insoluble in chloroform (β), 12·34; soluble in both pyridine and chloroform (γ), 6·12. The γ-compounds contained: Soluble in light petroleum (γ_1), 1·53; soluble in ethyl ether (γ_2), 1·46; residue (γ_3 and γ_4), 3·14 (all expressed as percentages on the ash-free dry coal).

Table I records the production of gaseous and liquid distillates by successive stages up to 550°.

The gases evolved up to 100° were mainly the higher paraffins. No marked increase in the rate of evolution of gases occurred up to 300°, but the proportion of paraffins decreased and that of oxides of carbon increased. Hydrogen was first noticed in the gases evolved over the range 300—320°, but even at 350° the gases contained no more than 1% of hydrogen, the fraction collected over the range 320—350° consisting mainly of the paraffins (ratio C/A on explosion analysis, 1·50), with about 10% of higher olefines. At 300°, hydrogen sulphide first made its appearance, a mobile oil, condensed at $-80°$, with a pungent garlic-like odour being evolved simultaneously.

The coal, which had previously been exhausted at room temperature during 4 days, lost 5% by weight of moisture up to 100°. This is not recorded as a product of distillation in Table I. Very little water was evolved between 100° and 300°. The "light oils"

TABLE I.

Distillation Products of Wigan Six Foot Coal.

(Liquid products expressed as per cent. by weight on ash-free dry coal.)

Temp. up to	100°	200°	250°	300°	320°	350°	400°	550°
Total gas (c.c. per 100 g. of coal)	40	127	150	178	602	1772	(not measured)	
Water	—	*0·12*	*0·16*	*0·29*	*0·79*	*2·09*	*4·09*	*5·39*
Light oils	Nil	0·04	0·10	0·35	0·57	1·30	2·31	2·70
Heavy oils	,,	Nil	0·23	1·33	3·24	8·79	10·90	10·99
Fractionation of heavy oils.								
Sat. hydrocarbons	—	—	0·19	0·70	0·99	1·75	2·06	2·06
Unsat. hydrocarbons	—	—	0·04	0·46	1·50	3·35	3·72	3·80
Phenolic and acidic oils	—	—	—	—	0·37	1·72	1·94	1·94
Ether-sol. oils	—	—	—	0·07	0·09	0·85	1·24	1·24
Chloroform-sol. oils	—	—	—	0·06	0·08	0·26	0·35	0·35
Bases	—	—	—	—	Trace	0·12	0·55	0·55
Loss during fractionation	—	—	—	0·04	0·21	0·74	1·04	—

were noticed first at 150° and the "heavy oils," condensing at atmospheric temperature, at 225°. The first runnings of heavy oils were mobile and of a red colour. They continued to be of this character up to 300°, very little gas being evolved meanwhile. At 318°, there was a sudden acceleration in the production of gases, water, and oils. At this temperature, phenolic and acidic compounds were noticed in the oils for the first time, but the bulk consisted of unsaturated hydrocarbons. At 330°, oils of another type were distilled simultaneously with the hydrocarbons. These were viscous and insoluble in light petroleum but soluble for the most part in ethyl ether. The production of heavy oils ceased at about 390°, the greater proportion being distilled over the range 300—375°. Light oils continued to be evolved in small quantities above 400° and water up to 550°, the highest temperature employed. Analyses of different fractions of the heavy oils are given in Table II, comparison being made with the γ_1 and γ_2 extracts of the original coal.

TABLE II.

Analyses of Oil Fractions.

Material.	Per cent. on ash-free dry coal.	Carbon %.	Hydrogen %.
{ Total heavy oils up to 300°	1·33	87·3	9·25
{ γ_1 extract from the coal freed from resins	1·20	86·5	9·10
{ Sat. hydrocarbon oils up to 300°	0·70	86·8	10·10
{ Sat. hydrocarbon oils from γ_1 extract	0·76	86·4	10·50
{ Ether-soluble portion of oil first evolved at 330°	1·24	81·8	7·02
{ γ_2 extract from the coal	1·46	81·6	6·40

The amount of γ_1-extract from the coal was 1·53%. The removal of resinous compounds by Robinson's method (J., 1925, **127**, 768) left 1·20% of a hydrocarbon oil. Both in quantity and in composition this oil corresponded closely with the " heavy oil " distilled from the coal up to 300°. Moreover, both the distilled oil and that removed from the coal by solvents lost 40% by weight on treatment with concentrated sulphuric acid, and from the saturated hydrocarbons remaining, of both oils (see Table II), a white solid hydrocarbon, m. p. 56—58°, was obtained by precipitation on cooling from boiling acetone. This close similarity (and the fact that very little gas accompanied the oils distilled from the coal) suggests that the primary oil obtained below 300° was yielded, without decomposition, by the γ_1-fraction. With all the coals we have examined in this manner there is close correspondence, both in quantity and in composition, between the hydrocarbon oils distilled from the coals below 300° and the γ_1-extracts (freed from resinous compounds).

The viscous oil that first made its appearance at 330° could be separated from the hydrocarbons by treatment with light petroleum and ethyl ether. On evaporation of the solvent, a red-brown solid was obtained similar in composition and general character to the resinous γ_2-extract from the coal. The quantity of this resinous material distilled from the Wigan Six Foot coal approximated to that of the γ_2-fraction, but with other coals the quantity may be considerably less.

Two fractions of the primary liquid distillation products of bituminous coal can thus be identified with the γ_1 (hydrocarbon) and γ_2 (resinic) constituents that are removed from the coal by solvents, and can be regarded as having been liquated from the coal conglomerate, not produced by decomposition of the coal substance. The thermochemical decomposition point of the coal is marked by a copious evolution of gases and water and by the appearance of phenolic and acidic compounds. With the Wigan Six Foot coal this thermochemical decomposition point was 318°. The work of Jones and Wheeler (J., 1914, **105**, 140) shows that the phenolic compounds are products of decomposition of the ulmin portion of the coal exclusively. They are accompanied by much gas and water.

Examination of Residues from Distillation of Wigan Six Foot Coal.—In view of the close correspondence between the γ_1 (hydrocarbon) and γ_2 (resinic) fractions, extractable from the Wigan Six Foot coal by solvents, and certain portions of the oils obtained on distillation of the coal, it was considered desirable to examine the solid residues remaining after distillation at different temperatures, more particularly as to their contents of substances extractable by solvents.

To this end a series of distillations of different charges of the same coal was carried out, in the manner already described, heating being stopped at 250°, 280°, 300°, 320°, and 350°, respectively. Each residue, after being washed with chloroform in the cold to remove traces of liquid distillates that might be adhering to it, was subjected to "solvent analysis" according to the scheme outlined by Cockram and Wheeler. The results are in Table III.

TABLE III.

Solvent Analysis of Distillation Residues.

(Per cent. on original coal, ash-free dry.)

	Insol. in pyridine.	Sol. in pyridine. Insol. in chloroform.	Sol. in chloroform.	Sol. in light petroleum. (Soluble in chloroform.)	Sol. in ethyl ether. (Soluble in chloroform.)	Insol. in light petroleum and ethyl ether. (Soluble in chloroform.)
Original coal ...	81·54 (α)	12·34 (β)	6·12 (γ)	1·53 (γ_1)	1·46 (γ_2)	3·14 ($\gamma_3+\gamma_4$)
Residue at 250°	86·31	8·79	4·90	1·33	1·64	1·93
„ 280°	87·48	8·12	4·40	0·91	1·82	1·67
„ 300°	87·71	8·25	4·04	0·58	1·95	1·51
„ 320°	84·35	10·08	5·57	0·52	2·10	2·95
„ 350°	92·28	5·73	1·99	0·19	0·78	1·02

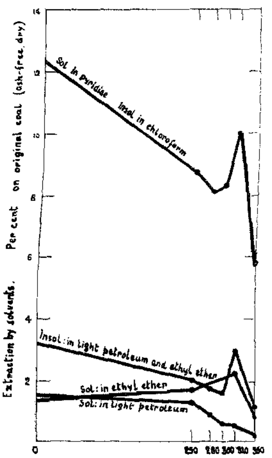
The general character of the changes that have taken place during the distillations is shown in Fig. 2. The residue after distillation at 300° contained but a small quantity of material extractable by light petroleum after fractionation with pyridine and chloroform (*i.e.*, material corresponding with the γ_1-fraction of the original coal). This, on examination by Robinson's method, was found to be wholly resinic. Corresponding, therefore, with the liquid hydrocarbons collected from the distillation at this temperature, the coal residue is devoid of an equivalent amount of material of like nature which, before the coal was heated, could be extracted from it by solvents. This, coupled with the fact, already recorded, that but little gas is evolved at this temperature, is strong presumptive evidence that the oils distilled were originally present, as such, in the coal. Additional evidence is afforded by the fact that the hydrocarbon oils collected from the distillation of the coal up to 300° can be redistilled unchanged (in a vacuum) over a temperature range but little lower than that at which they were distilled from the coal.

Heating at each stage up to 320° caused in the residues an increase in the amounts of extracts corresponding with the γ_2-fraction of the original coal. This was probably derived from the resin-like constituents originally soluble only in chloroform or acetone (the γ_3- and γ_4-fractions), since the effect of moderate heat on them is

to render them in part soluble in ethyl ether, when they are recognisable as resins.

The residue after heating at 350° had lost most of the original ether-soluble material (γ_2-fraction), and, as already recorded, an identical material first appeared in the liquid distillation products just below this temperature (at 330°) and could be separated from them as a red-brown solid. The source of this solid is thus the extractable resins of the coal, but complete distillation of the resins, unchanged, from the coal cannot be presumed (as it can with the hydrocarbons), for with the majority of coals less is obtained by distillation than by extraction. Moreover, this resinous distillate from the coal cannot be re-distilled unchanged. On distillation at 400° in a vacuum, for example, the distillate amounts to about 70% of the original, is more fluid and is soluble (60%) in light petroleum, and the undistilled residue is soluble in chloroform.

FIG. 2.



Temperature at which coal was distilled, °C.

Two observations suggest the manner in which this resinous distillate is yielded by the coal. When the duration of heating was much prolonged, the temperature at each stage being maintained during 720 instead of the usual 120 hours, a quantity of the ether-soluble resin was present in the distillate at a rather lower temperature than before (at 310°), and some could be washed out of the residual coal charge with cold chloroform, suggesting that the first action of heat on the resinic constituents of the coal was to liquate them to the surface of the coal particles. Further, when a number of coals are examined in the manner described in this paper, it is found that the relationship between the quantity of resins extractable from the coal by solvents and obtained from them by distillation is dependent on the amount of hydrocarbon oil that accom-

panies them. The greater the quantity of hydrocarbon oil distilled from the coal, the nearer does the quantity of resins distilled correspond with the quantity extractable from the original coal by solvents. The suggestion is that, during the heating of the coal, the resins are first melted and then in part carried away by the hydrocarbon oil vapours that are being distilled at the same time. No doubt such of the resins as are not vapour-distilled in this manner are later decomposed or modified by the heating in much the same manner as they are found to be on redistillation, becoming mobile and for the most part soluble in light petroleum.

The thermochemical decomposition point of the coal is sharply defined and is unaltered by changes in the experimental conditions. With the Wigan Six Foot coal the decomposition point is 318° whether the distillation is effected in a vacuum or at atmospheric pressure. Heating during one month at 310° causes no appreciable decomposition.

Marked by a copious evolution of gases, water, and oils, the decomposition point of a coal is the beginning of the breakdown of the ulmin constituents (the major part of the coal), and thereafter the effect of heat is to produce profound changes in the coal substance. These changes, apparent on examination of the solid distillation residues, affect not only the behaviour of the coal towards solvents (see Fig. 2) but its reactivity in general (with oxygen, for example) and its caking power. A further communication, in which the decomposition points of a number of coals are compared, will deal with this subject more fully.

Whilst the characteristic liquid products of destructive distillation of the ulmin portion of the coal are phenolic and acidic compounds, hydrocarbon oils are also produced and contribute to the yield of such oils obtained on heating the coal above its decomposition point. For the most part, however, the hydrocarbon oils obtained over the higher temperature ranges are derived from the organised plant entities (mainly spore exines and cuticular tissues) preserved in the coal. Details of the researches on which this conclusion is founded will be given later.

The work described in this paper forms part of a research on the constitution of coal which we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish the results.

SAFETY IN MINES RESEARCH LABORATORIES,
SHEFFIELD. [Received, August 3rd, 1928.]

CCLIII.—*A Synthesis of Behenolic Acid.*

By RAMAKANTA BHATTACHARYA, SHANKAR RAO SALETORE, a
JOHN LIONEL SIMONSEN.

AN analytical investigation led Mirchandani and Simonsen (J., 19
371) to conclude that *iso*erucic acid is an inseparable mixture Δ^{11}-*heneicosene*-1-*carboxylic acid* (I) and Δ^{13}-*heneicosene*-1-*ca oxylic acid* (II).*

$$CH_3\cdot[CH_2]_8\cdot CH\colon CH\cdot[CH_2]_{10}\cdot CO_2H \quad (I.) \qquad CH_3\cdot[CH_2]_6\cdot CH\colon CH\cdot[CH_2]_{12}\cdot CO \quad (II.)$$

Syntheses of these two acids are desirable to establish this, b unfortunately the methods available for syntheses of this type a somewhat limited (compare Robinson and Robinson, J., 1925, **12** 175). The most direct method would appear to be the preparati of the corresponding acetylenic acids, since the reduction of the to the ethylenic acids is readily performed, and we decided explore first the synthesis of behenolic acid (III).

$$\underset{(IV.)}{C_8H_{17}\cdot C\colon CNa} + \underset{(V.)}{CH_2Br\cdot[CH_2]_{10}\cdot CO_2Me} \longrightarrow CH_3\cdot[CH_2]_7\cdot C\colon C\cdot[CH_2]_{11}\cdot CO_2H \text{ (III)}$$

The method adopted was the condensation of the sodium derivati of decinene (IV) with *methyl* 11-*bromododecoate* (V). Decinene w prepared by Picon's method (*Compt. rend.*, 1919, **169**, 32) fro octyl iodide and sodium acetylide: we have found that the reactio proceeds best at 180°. For the synthesis of the bromo-este decane-1 : 10-dicarboxylic acid was prepared in considerab quantity by Walker and Lumsden's method (J., 1901, **79**, 1191) their methods for the preparation of 10-bromoundecoic acid an its conversion into the dibasic acid have both been improved.

Methyl hydrogen decane-1 : 10-*dicarboxylate*, obtained by th partial hydrolysis of the dimethyl ester, was reduced to 11-*hydroxy dodecoic acid*, m. p. 78—79°, by the method of Grün and Wirt (*Ber.*, 1922, **55**, 2216). This acid does not appear to be identic with any of the hydroxydodecoic acids previously described. I was thought that it might be identical with the acid isolated b Power and Rogerson from *Ipomœa purpurea* (*Amer. J. Pharm.* 1908, **80**, 251), but direct comparison with a specimen of this acid for which we are much indebted to Dr. T. A. Henry, showed thi not to be the case. The hydroxy-acid, when treated with hydroge bromide in methyl-alcoholic solution, was converted into th

* In the paper referred to (p. 373), the acids (I) and (II) are wrongly name as derivatives of docosene.

required bromo-ester. Although this crystallised well, we have not succeeded in obtaining it quite pure. Condensation of sodiodecinene and methyl 11-bromododecoate in xylene at 160° resulted in the formation of a liquid ester which, on hydrolysis, gave an acid crystallising from methyl alcohol in needles, m. p. 57°, identical in all respects with a specimen of behenolic acid prepared from erucic acid.

EXPERIMENTAL.

10-*Bromoundecoic Acid*.—To a mechanically stirred and well-cooled solution of hydrogen bromide in toluene (HBr, 10—15%) the requisite amount of undecylenic acid was gradually added. After 2—3 hours, the bromo-acid, which had crystallised (m. p. 51°), was collected; a further quantity could be obtained by cooling the filtrate in a freezing mixture. The bromo-methyl ester, b. p. 165°/10 mm., prepared by the action of methyl alcohol and sulphuric acid (Found: Br, 28·2. Calc.: Br, 28·7%), was converted into the cyano-ester (b. p. 180°/10 mm.) by digestion for 2 hours with an alcoholic solution of potassium cyanide. On hydrolysis, the cyano-ester gave an excellent yield of decane-1 : 10-dicarboxylic acid: this is a more convenient method than that described by Walker and Lumsden (*loc. cit.*) for the preparation of this acid.

Methyl Hydrogen Decane-1 : 10-*dicarboxylate*.—Methyl decane-1 : 10-dicarboxylate, b. p. 170°/10 mm. (Found: C, 65·5; H, 10·0. Calc.: C, 65·1; H, 10·1%) (compare Chuit, *Helv. Chim. Acta*, 1926, **9**, 264), was converted into the hydrogen ester by the method of Grün and Wirth (*loc. cit.*, p. 2215) or by partial hydrolysis with cold alkali. The yield was in both reactions poor. The dibasic acid and the hydrogen ester were separated by treatment with light petroleum, in which the former was very sparingly soluble. *Methyl hydrogen decane*-1 : 10-*dicarboxylate* crystallised from methyl alcohol in prisms, m. p. 51° (Found: C, 63·5; H, 10·0. $C_{13}H_{24}O_4$ requires C, 63·9; H, 9·8%).

11-*Hydroxydodecoic Acid*.—To a mechanically stirred suspension of finely divided potassium methyl decane-1 : 10-dicarboxylate (dried over phosphoric oxide) in boiling absolute alcohol (10—12 parts), sodium (4 times the theoretical quantity) was added as rapidly as possible. After 1 hour, dilute alcohol and water were added and the mixture was heated to hydrolyse the ester. The excess of alcohol was removed with steam, and hydrochloric acid added until the solution was faintly alkaline. After extraction with ether to remove neutral reduction products, magnesium sulphate was added; the magnesium salt of the hydroxy-acid was then precipitated. This was collected and decomposed with hydrochloric acid and the hydroxy-acid obtained was converted once more into

the magnesium salt. The acid now regenerated from the magnesium salt still contained an appreciable quantity of the dibasic acid which could not be readily separated by crystallisation. The crude acid was therefore boiled with acetyl chloride, the excess of acetyl chloride removed on the water-bath, and the mixture of 11-acetoxydodecoic acid and decane-1 : 10-dicarboxylic acid separated by treatment with light petroleum, in which the former was readily soluble. The acetylated acid was a wax which did not lend itself to purification. It was hydrolysed with alkali and the *hydroxy-acid* was repeatedly crystallised from light petroleum (b. p. 60—80°) and finally from dilute methyl alcohol; it was then obtained in needles, m. p. 78—79° (Found: C, 66·4; H, 10·9. $C_{12}H_{24}O_3$ requires C, 66·7; H, 11·1%).

The *magnesium* salt, which was very sparingly soluble in water, was an amorphous, white solid (Found: Mg, 5·0. $C_{24}H_{46}O_6Mg$ requires Mg, 5·3%). The methyl ester had b. p. 160°/7 mm. and the anilide crystallised from light petroleum in small prisms, m. p. 87°.

Methyl 11-*Bromododecoate.*—The hydroxy-acid, dissolved in four parts of methyl alcohol, was saturated with hydrogen bromide and after digestion on the water-bath for 3 hours the methyl alcohol was removed in a current of hydrogen bromide. The residue, which crystallised, was dissolved in ether, and the ethereal solution was washed with sodium carbonate solution to remove any acid present, dried, and evaporated. The *bromo-ester* crystallised from methyl alcohol in fatty needles, m. p. about 50°, which was not altered by recrystallisation. Analysis showed the ester to be still somewhat impure (Found: Br, 23·3. $C_{13}H_{25}O_2Br$ requires Br, 27·3%).

Decinene.—Into a suspension of sodamide (from 5 g. of sodium) in liquid ammonia (Hess and Munderloh, *Ber.*, 1918, **51**, 377), acetylene was passed until complete conversion into sodium acetylide had taken place, the temperature being maintained at −60° to −45° by means of liquid air. Octyl iodide (50 g.) having been added, the mixture was allowed gradually to attain room temperature, the ammonia evaporating. After 12 hours, the temperature was maintained at 180° for 8—10 hours. Water was added to the cooled mixture, and the decinene separated by distillation in steam. The hydrocarbon was washed with dilute sulphuric acid to remove basic impurities and distilled; the greater portion passed over at 175—180°/685 mm. ($d_{20°}^{20°}$ 0·799, $n_D^{20°}$ 1·44) and was sufficiently pure for conversion into the sodium derivative.

Condensation of Sodiodecinene and Methyl 11-*Bromododecoate.*—To finely divided sodium (0·25 g.), in an atmosphere of hydrogen, decinene (2·g.) was gradually added, the formation of the sodium

ompound being hastened by gentle heating. After the addition f the bromo-ester (3·4 g.) in xylene the mixture was heated at 60° for 8 hours. Water was added to the cooled solution, and the ylene and the excess of decinene were removed in steam; the esidual oil was dissolved in ether, the ethereal solution washed with odium carbonate solution, and the solvent evaporated. The thick, ly residue was hydrolysed with methyl-alcoholic potassium ydroxide; the acid, isolated in the usual manner, partly crystallised n keeping. After draining on porous porcelain, it was recrystallised om methyl alcohol, behenolic acid being obtained in glistening eedles, m. p. 57°. It was carefully compared with a specimen of *ehenolic acid prepared from erucic acid, and a mixture of the two* cids had m. p. 56·8—57° (Found: C, 78·3; H, 11·6. Calc.: , 78·5; H, 11·9%). The barium salt also was analysed (Found: a, 17·2. Calc.: Ba, 17·0%).

One of us (J. L. S.) wishes to thank Professor C. S. Gibson, O.B.E., or the provision of facilities in his laboratory for carrying out some f the experiments detailed above.

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CCLIV.—*Polysaccharides. Part II. The Acetylation and Methylation of Starch.*

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XPERIMENTS have been instituted to render more accessible and characterise the acetyl and methyl derivatives of starch. In the esent work purified potato starch has been employed. Hitherto e yields of both triacetyl and trimethyl starch do not appear to ave been satisfactory.

Since Schützenberger's original experiments (*Compt. rend.*, 1865, 1, 485; 1869, **68**, 814) many investigators have attempted to epare triacetyl starch. If unmodified starch be employed, the ansformation is generally held to be difficult and uncertain, and e small yields lead to serious doubt whether the product is an etyl derivative of the unchanged starch or is derived from a rtion only of polysaccharide which has been segregated during e process of acetylation.

More success has attended the acetylation of a starch which has en subjected to various preliminary treatments. Soluble starch,

for example, has been converted into the triacetyl derivative (Pre[
Monatsh., 1901, **22**, 1049); and the acetylation of the separat
amylose constituent of potato starch may readily be effected in t
presence of pyridine (Bergmann and Knehe, *Annalen*, 1927, **45**
141). Such processes, however, not only involve considerable lo
during the initial treatment of the polysaccharide, but in ma
cases suffer also from the disadvantage that the relationship betwe
the original starch and the final product is by no means clear.

We have endeavoured, therefore, to obtain an acetylated deri
ative of starch in the maximum possible yield and under the simple
experimental conditions. In this way, we consider, informatio
respecting the acetylation of the whole of the starch may be gaine
and the properties of the starch acetate may then be compared wit
those of the known acetylated products isolated by less direc
methods and in inferior yield.

Preliminary experiments conducted by the methods of E. Peise
(*Z. physiol. Chem.*, 1926, **161**, 210) failed to give, even in sma
yield, the acetylated starch of high specific rotation claimed t
have been obtained by that author (compare also Pringsheim an
Meyersohn, *ibid.*, 1928, **173**, 211). We are in agreement, however,
with Peiser that the preliminary precipitation of starch from starch paste by alcohol yields a product which is much more susceptible to acetylation than the original starch, from which it appears to differ only in being more finely divided as the result of the bursting of the granules; *e.g.*, it retains unimpaired the properties of acquiring a deep blue colour on treatment with iodine and of readily giving a paste. Whereas Bergmann and Knehe (*loc. cit.*) conducted the acetylation of separated amylose in the presence of pyridine, we have employed traces of sulphur dioxide and chlorine as catalysts, and we have obtained from precipitated starch a triacetyl derivative in a yield of 96% of the theoretical, based on the weight of the original unmodified starch. Our product is compared below with Bergmann and Knehe's triacetyl amylose:

	Triacetyl starch.	Triacetyl amylose.	Calc.
$[\alpha]_D$ (in chloroform) ...	+170° at 20°	+176° at 16°	—
C, %	49·8	50·0	50·0
H, %	5·8	5·7	5·6
$CH_3 \cdot CO$, %	44·4	44·6	44·8

The triacetyl starch differed little, if at all, in its properties from the product of Bergmann and Knehe. It gave on deacetylation a regenerated starch having all the properties of the regenerated amylose of those authors, being soluble in water and giving the characteristic blue colour with iodine. Both in the precipitated starch and in the triacetyl derivative the presence of traces of

phosphoric acid residues was detected. The deacetylation process almost necessarily involves the scission of the phosphoric ester linkages, and according to the views of Samec and Mayer (*Kolloidchem. Beih.*, 1921, **13**, 284) on the relationship between amylose and amylopectin the loss of the phosphoric residues must result in the formation of a starch which is incapable of producing a paste with water. This we found to be the case with our regenerated polysaccharide, and the present results have therefore a bearing on the relationship of amylose to amylopectin. It appears that potato starch reacts chemically to the extent of 96% at least as if it were amylose, and our experiments tend to confirm the views of Samec and Mayer. This question will be dealt with in greater detail in a further communication.

Experiments on the methylation of starch have been described by several authors, including Karrer (*Helv. Chim. Acta*, 1920, **3**, 620) and Irvine and Macdonald (J., 1926, 1502). The method adopted by these authors was to act on the original starch with methyl sulphate and alkali and in each case the yield of methylated starch was small; Irvine and Macdonald, *e.g.*, obtaining from 24 methylation treatments a yield of 25% of trimethyl starch. We have obtained, after only six methylations, 89% of the theoretical yield of trimethyl starch by taking advantage of the solubility of triacetyl starch in acetone. The addition of methyl sulphate and dilute alkali to such a solution introduced in one operation 36% of methoxyl, and a progressive increase of the methoxyl content was obtained on each subseqnent methylation.

The product appears to be identical with the material described by Irvine and Macdonald, who operated with both rice and potato starch. Hydrolysis of the trimethyl starch with 2% hydrogen chloride in methyl alcohol yielded 80% of pure trimethyl methylglucoside and 8% of a mixture of the latter with dimethyl methylglucoside, leaving a residue of 6% which was not hydrolysed. Hydrolysis of the trimethyl methylglucoside gave crystalline 2 : 3 : 6-trimethyl glucose (yield, 85%) and there can therefore be no doubt that nearly the whole of the potato starch gives rise on methylation and hydrolysis to 2 : 3 : 6-trimethyl glucose.

This conclusion has considerable significance in showing that the mode of linking of the glucose units in potato starch leaves three exposed hydroxyl groups at analogous positions to those which have been determined in the case of cellulose. The specific rotations of trimethyl starch (+ 208°) and trimethyl cellulose (— 18°) are, however, widely different.

By dispensing with the use of acetone as solvent for the triacetyl starch during the methylation, we have prepared a dimethyl starch

(yield, 80% of the theoretical) having $[\alpha]_D + 143°$ in chloroform and OMe, 31·8%. This again appeared to be similar to the dimethyl starch described by Irvine and Macdonald. We were unable, however, with our product to confirm the observation of these authors that this is a homogeneous substance yielding on hydrolysis only dimethyl glucose. Our product gave on hydrolysis a mixture of trimethyl, dimethyl, and monomethyl glucose. The trimethyl glucose was present to the extent of about 20%. The results indicate that all the hydroxyl groups are exposed to simultaneous attack by the methylating agents. In this respect there would appear to be no well-marked difference between the phenomena observed in the methylation of starch and of cellulose. The problem is rather one of obtaining the polysaccharide initially in a suitable condition for combination with the methylating agent. In the present case we have found that after three methylation treatments the starch has acquired a methoxyl content of 40% or more; and similarly with cellulose, Freudenberg and Braun (*Annalen*, 1928, **460**, 288) have observed that the introduction of 42% methoxyl content can be accomplished by two treatments with methyl sulphate if the cellulose fibres used are diminished to 2—4 mm. in length. In the earliest experiments of Denham and Woodhouse (J., 1914, **105**, 2363) a methylated cellulose of about 25% methoxyl content gave an appreciable proportion of trimethyl glucose on hydrolysis. The increase in the methoxyl content of starch from 38 to 44% proceeds just as easily and regularly as from 34 to 38% (contrast Irvine and Macdonald). We are doubtful, therefore, whether the claim can be substantiated that seven out of nine hydroxyl positions in starch undergo preferential methylation. If maltose is preformed in starch, then the polysaccharide is composed of glucopyranose units joined in positions 1 : 4. The alternative hypothesis is that maltose is a reversion product and that starch is composed of glucofuranose units linked in positions 1 : 5. These opposing views will be the subject of subsequent work.

EXPERIMENTAL.

Acetylation of Starch.—The starch used in these experiments was the purest commercial potato starch (Prime starch), the properties of which corresponded in all respects with those ascribed in the literature to pure potato starch. It contained 18% of water.

It was prepared for acetylation in the following manner. The starch (20 g.) was stirred in water (600 c.c.) on the water-bath until it formed a paste. After 30 minutes the heating was discontinued and the starch was precipitated by the addition of alcohol to the warm paste. The supernatant liquor was decanted from the white

curdy mass which soon settled, and the starch was ground in a mortar in the presence of alcohol. It was then washed with alcohol and ether and dried in a vacuum desiccator (yield, quantitative). This process resulted in the bursting of the granules of the original starch but in general respects appeared to be without effect on its properties. The ash content (0·3%, by incineration), the paste-forming capacity, the blue iodine colour reaction, and the absence of reducing power were all reproduced in the prepared starch.

Attempts to acetylate potato starch by the usual methods revealed many unsatisfactory features, but the following process, which is a modification of Barnett's method (*J. Soc. Chem. Ind.*, 1921, 40, 8T) for the acetylation of cellulose, was found to be eminently suitable for the routine preparation of the triacetate. Finely powdered starch (prepared in the above manner) was treated with six times its weight of glacial acetic acid through which chlorine had been bubbled for a few seconds. The mixture was stirred for 30 minutes at 20°. Acetic anhydride (20 parts by weight), containing an amount of sulphur dioxide equivalent to that of the chlorine in the acetic acid, was then added and the mixture was stirred at room temperature for 60 minutes. The temperature was then raised to 55° and stirring was continued until a clear solution was obtained (about 4 hours). The clear solution was poured into a large excess of water, and the resulting white powder was washed for some 2 days with changes of water and, when free from acid, successively with dilute alcohol, alcohol, and ether; it was then dried for twenty-four hours in a vacuum (yield, 96·5% of the theoretical). This material contained neither chlorine nor sulphur. It was a white impalpable powder, without action on boiling Fehling's solution, insoluble in ether, alcohol or water, but readily soluble in chloroform and in acetone. The acetate could be reprecipitated unchanged from its solutions in the last two solvents by the addition respectively of alcohol and water. When the acetate was treated with aqueous or alcoholic sodium hydroxide solution, the regenerated starch possessed all the properties of Bergmann's regenerated amylose. Hydrolysis of the acetate by the method of Bergmann and Knehe (*loc. cit.*) gave a white powder, soluble in cold water, $[\alpha]_D^{17°} + 186°$ ($c = 1·0$). This gave a blue colour with iodine, but did not form a paste with hot water. For the starch acetate the following data were observed: $[\alpha]_{5461}^{20°} + 197°$ in chloroform ($c = 1·0$); $[\alpha]_D^{20°} + 170°$ in chloroform ($c = 1·0$). The air-dry acetate contained 2·2% of moisture. Acetyl estimations were carried out by treating a weighed quantity with an excess of $N/2$-alcoholic sodium hydroxide for 3 hours at 50°, with

frequent shaking (Found : C, 49·8 ; H, 5·8 ; CH_3·CO, 44·4 ; P, P_2O_5, 0·05. $C_{12}H_{16}O_8$ requires C, 50·0 ; H, 5·55 ; CH_3·CO, 44·8%

Acetylation of the prepared starch may be effected at tei peratures higher or lower than the 55° mentioned, without affecti in any way the chemical properties or the specific rotation of t starch acetate. Too low a temperature, however, involves pr longed treatment. The principal difference between the vario samples of acetate obtained at different temperatures appeared lie in the greater viscosity of the acetate solutions obtained . lower temperatures.

It is to be noted that careful preparation and drying of tl "prepared" starch are essential. Certain specimens of prepar starch which had been heated at 80° to complete the drying proce were found to acetylate slowly and imperfectly, the retardation beir due apparently to alteration of surface conditions produced by hea

For comparison, acetylations were also carried out on the origin starch (before preparation), (*a*) chlorine and sulphur dioxide, a above, and (*b*) sulphuric acid being used as catalysts. In (*a*) it wa found impossible to effect complete solution of the starch eve after 12 hours at 65° with high concentrations of catalyst. Afte removal of the undissolved starch by filtration through glass woo the acetylated starch was isolated in the manner already describec The product was essentially similar to that from prepared starc but had a lower specific rotation, $[\alpha]_D$ + 154° in chloroform (c = 1·0) The yield (15% of the theoretical) was very inferior to that of th first method.

In case (*b*) 10 g. of starch and 60 c.c. of acetic anhydride con taining 12 drops of sulphuric acid were heated at 55° for 8 hours The brown liquid was filtered through glass wool, and the produc isolated as before. The resulting acetate showed $[\alpha]_D$ + 169° ir chloroform (c = 1·0) and appeared to be identical with the materia obtained from the prepared starch. The yield, however, was smal (10—15%), much of the starch either decomposing or not under going acetylation.

Methylation of Potato Starch.—Preliminary experiments, followin the methods of Irvine and Macdonald (*loc. cit.*), confirmed the grav manipulative difficulties encountered in the direct methylation o starch. When, however, a method of simultaneous deacetylation and methylation was used, these difficulties almost entirely disappeared. This was peculiarly the case when the operations were conducted in acetone solution. If the following procedure is adopted, methylation of starch becomes sufficiently rapid and convenient to render methylated starch the most suitable intermediate substance for the preparation of 2 : 3 : 6-trimethyl glucose.

(a) *Methylation in presence of water only.* Powdered starch triacetate (20 g.) was treated with 30% sodium hydroxide solution (224 c.c.) and methyl sulphate (80 c.c.), added gradually and simultaneously with vigorous mechanical stirring. The temperature was maintained at 50° for $1\frac{1}{4}$ hours and thereafter at 70° for a further $1\frac{1}{4}$ hours until the whole of the reagents had been added, care being taken to avoid acidity at any stage. After being heated for 30 minutes at 100°, the solution was cooled, rendered almost neutral by addition of 30% sulphuric acid, and filtered. The solid residue was extracted with boiling chloroform. The slightly alkaline aqueous portion was treated with excess of carbon dioxide and evaporated to dryness in the presence of barium carbonate, and the solid residue extracted with chloroform. The united chloroform extracts yielded (when evaporated) a white flaky solid, which was slightly soluble in water or chloroform and had a methoxyl content only slightly lower than that reqnired by a dimethyl starch. Yield, 80% of the theoretical for dimethyl starch. $[\alpha]_D + 143°$ in chloroform ($c = 1·0$) (Found: OMe, 31·8. Dimethyl starch requires OMe, 32·7%).

Hydrolysis of dimethyl starch. The methylated starch (4·0 g.) was dissolved in methyl alcohol (50 c.c.) containing 2% of hydrogen chloride and the solution was boiled for 24 hours. The acid was neutralised by addition of lead carbonate, and the product isolated in the usual way. It was a viscous syrup (4·55 g.) which, on distillation, gave (I) 0·9 g., b. p. 110—117°/0·05 mm., $n_D^{16°}$ 1·4611 (Found: OMe, 47·7%); (II) 1·45 g., b. p. 117—130°/0·04 mm., $n_D^{16°}$ 1·4670 (Found: OMe, 41·5%); (III) 1·48 g., b. p. 130—180°/0·03 mm., $n_D^{16°}$ 1·4800 (Found: OMe, 37·2%); (IV) still residue, 0·6 g. Dimethyl methylglucoside and trimethyl methylglucoside require respectively OMe 41·9% and 52·6%. The distillates were glucosidic in character; (I) appeared to consist mainly of trimethyl methylglucoside, and (II) and (III) mainly of dimethyl methylglucoside admixed with some monomethyl methylglucoside. This diagnosis was confirmed in the case of (I) by hydrolysing it with boiling 5% aqueous hydrochloric acid for 4 hours. The acid was neutralised with barium carbonate, the neutral solution evaporated to dryness at 50°/15 mm., and the product of hydrolysis extracted from the solid residue by boiling ether. Removal of the ether left a syrup which crystallised almost completely (yield, 80%). Recrystallisation from ether removed some adhering gum and gave in good yield 2 : 3 : 6-trimethyl glucose, m. p. 117—118°; mixed m. p. with a specimen of 2 : 4 : 6-trimethyl glucose of m. p. 124°, 90—95°. No tetramethyl glucose was present.

Further methylations by the same method gave a pro-

gressive increase in the methoxyl content. This applied also to the simultaneous deacetylation and methylation of the acetylated methylated starch obtained by heating dimethyl starch with acetic anhydride and fused sodium acetate at 100° for 1½ hours (compare Irvine and Macdonald, *loc. cit.*). Methylation by means of Purdie's reagents was ineffective and was known to lead to changes in the nature of the methylated starch.

(b) *Methylation with acetone as solvent.* The process (a) yielded a dimethyl starch readily and in good yield, but constituted no improvement on known methods for proceeding from dimethyl starch to the fully substituted derivative. The following method gives in one operation a methylated starch with a methoxyl content of 36%, greatly reduces the manipulative difficulties, and facilitates the preparation of trimethyl starch in almost quantitative yield. It consists essentially in the simultaneous deacetylation and methylation of starch triacetate dissolved in acetone in a large flask provided with a reflux condenser, through which the spindle of the stirrer is passed. Efficient stirring is necessary. The methoxyl content of the product may be varied by employing a smaller quantity of acetone and in this way methylated starches containing from 28% to 36% OMe have been obtained.

Preparation of methylated starch (OMe, 36%). Powdered starch triacetate (25 g.) was dissolved in acetone (250 c.c.) and treated with 30% sodium hydroxide solution (280 c.c.) and methyl sulphate (100 c.c.). The methylating reagents were added (with the usual precautions) in ten equal portions at intervals of 10 minutes, the temperature being maintained at 56°. After being heated for 30 minutes at 100°, during which the acetone was allowed to evaporate, the mixture was almost neutralised with sulphuric acid, treated with excess of carbon dioxide, and filtered. The aqueous portion was extracted four times with chloroform; * the solid was extracted with boiling chloroform. The combined extracts gave on evaporation a light yellow, glassy solid (16·8 g.; 96% of the theoretical). Further purification was effected by dissolving it in a little chloroform and boiling with excess of ether. This yielded a white impalpable powder which was dried at 100°/15 mm. The loss during this treatment was inappreciable. The dry substance showed $[\alpha]_D$ + 170° in chloroform. Ash (mainly sodium sulphate), 1·6%

* When methylated starches of methoxyl content 34% or more are being dealt with, the chloroform separates readily from the aqueous layer. Below 34% an intractable emulsion usually forms and more tedious methods have to be adopted (see above). With increasing methoxyl content manipulative difficulties of this kind progressively diminish.

(Found : C, 50·8 ; H, 7·7 ; OMe, 36·0. Calc. for methylated starch : C, 51·2 ; H, 7·6 ; OMe, 36·0%).

Two more methylations under similar conditions raised the methoxyl content by 4%. After three further methylations (being six in all) a product corresponding very closely to trimethyl starch was obtained. The final product was purified by dissolving it in a little chloroform and boiling the solution with excess of light petroleum. The crisp white powder obtained was treated again with light petroleum, separated by filtration, and dried in a vacuum (Found : OMe, 44·0 ; ash, 0·04%). The loss in yield on each methylation was 0·1 g., and the final yield of methylated starch from starch triacetate was thus 92% of the theoretical. This represents a yield of 89·4% of the theoretical from the original starch.

No advantage could be gained by introducing an acetylation process after the first methylation, the solubility of the methylated starch in acetone being apparently the decisive factor in facilitating the etherification. For instance, in one experiment the product from the first treatment of starch triacetate in acetone solution (yield, 16·4 g. from 25·0 g. Found : C, 50·4 ; H, 7·8 ; OMe, 34·4 ; ash, 0·9%) was acetylated by heating it with 8 parts of acetic anhydride and 1 part of fused sodium acetate for 1½ hours at 100°. The mixture was then poured into an excess of cold water, the acid neutralised with sodium bicarbonate, and the product extracted from the solution by chloroform (yield, 10 g. from 10 g. Found : $CH_3 \cdot CO$, 12 ; OMe, 30·6%). Simultaneous deacetylation and methylation in acetone, followed by a further acetylation and combined deacetylation and methylation, raised the methoxyl content to 36·4%. Four successive methylations in acetone solution then gave trimethyl starch (Found : OMe, 45%).

Trimethyl Starch and its Hydrolysis.—The methylated starch finally obtained was a white powder, m. p. 145° with previous softening, $[\alpha]_D$ + 208° in chloroform (c = 1·0), which appeared to be identical with the material described by Irvine and Macdonald (*loc. cit.*) (Found : C, 52·4 ; H, 7·9 ; OMe, 44·0 ;* ash, 0·04. Calc. for $C_9H_{16}O_5$: C, 52·9 ; H, 7·8 ; OMe, 45·5%). When boiled for 24 hours with methyl alcohol containing 2% of hydrogen chloride, it gave (*a*) pure trimethyl methylglucoside, b. p. 95—97°/0·02 mm., $n_D^{24°}$ 1·4550 (yield, 80%) (Found : OMe, 51·8. Calc. : OMe, 52·6%) ; (*b*) a mixture of trimethyl methylglucoside and dimethyl methylglucoside having $n_D^{24°}$ 1·4630, OMe 44% (yield, 8%) ; (*c*) a small

* As in the case of cellulose, the final 1% of methoxyl can be introduced only with great difficulty. In the present experiments methylation has not been carried beyond the stage 44—45%.

quantity of solid which appeared to be unhydrolysed materi (yield, 6%). Fraction (*b*) corresponded to the small amount dimethyl starch in the original material, the presence of which w indicated by the slight deficiency in the OMe value. Hydrolysis (*a*) with boiling 5% aqueous hydrochloric acid gave only 2 : 3 : 6-tr methyl glucose (yield, 85%), which, after one recrystallisation, ha m. p. 117° alone or when mixed with an authentic specimen of th same m. p. Tetramethyl glucose was definitely absent.

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CCCLV.—*Polysaccharides. Part III. The Molecular Complexity of Inulin.*

By HARRY DUGALD KEITH DREW and WALTER NORMAN HAWORTH.

IT is now generally accepted that inulin is composed entirely of anhydro-γ-fructose or -fructofuranose units associated with water molecules, the relative proportion of water depending upon the method of drying. For instance, Tanret (*Bull. Soc. chim.*, 1893, **9**, 200, 227, 622) regards inulin as $(C_6H_{10}O_5)_6,H_2O$ at 130° and as $(C_6H_{10}O_5)_6,7H_2O$ in moist air at the ordinary temperature. Other attempts to determine the number of anhydrofructose units in the inulin molecule have given very conflicting results. Karrer and Lang (*Helv. Chim. Acta*, 1921, **4**, 249), from a determination of the molecular weight of trimethyl inulin in freezing phenol, find nine anhydrofructose units, in agreement with the molecular weight of triacetyl inulin in naphthalene, glacial acetic acid, and phenol, as determined by Pringsheim, Aronowsky, and Lassmann (*Ber.*, 1921, **54**, 1281; 1922, **55**, 1409). Bergmann and Knehe (*Annalen*, 1926, **449**, 302; *Ber.*, 1926, **59**, 2079) find only two anhydrofructose units in acetyl inulin prepared in the presence of pyridine. Again, Hess and Stahn (*Annalen*, 1927, **455**, 104) find that triacetyl inulin as prepared by Bergmann and Knehe has in air-free acetic acid a (cryoscopically determined) molecular weight which varies with time from that corresponding with the presence of one anhydrofructose unit up to infinity. Later work of Pringsheim and Fellner (*Annalen*, 1928, **462**, 231) indicates that the molecular weight of "inulin," regenerated from inulin acetate heated at various temperatures in presence of tetrahydronaphthalene, is variable according

to the temperature of the heating, two, three, or four anhydrofructose units being present in the molecule. Direct determinations of the molecular weight of inulin in water are stated by these authors to agree in indicating that seven anhydrofructose units are present in the molecule.

It is clear that derivatives of inulin (such as the acetyl and methyl compounds) can throw no light on the complexity of inulin itself until it is demonstrated that these derivatives are simply related to the carbohydrate; and, although it has been alleged that inulin may be regenerated from the triacetyl compound, no definite proof of this statement has yet been given. Indeed, it has by no means been shown that inulin consists of uniform molecules.

Assuming that inulin consists of anhydrofructose units, these may be united either by residual affinities, in which case the structural units are retained as such in the complex, or by ordinary valencies, when the fructofuranose units are linked in chain formation. If the latter be true, as seems probable at present (compare Haworth and Learner, this vol., p. 619), the chain of γ-fructose (fructofuranose) units in the inulin molecule may be either open or closed to a ring. If it be an open chain, aqueous solutions of inulin should show slight reducing properties, due to the terminal reducing groups of the chains; if the ends of the chains be joined to give a ring, reduction may not be made manifest.

It has generally been held that pure inulin has no reducing action on hot Fehling's solntion, but we have not yet succeeded in obtaining a sample of inulin which did not show slight and progressive reducing action on the boiling reagent. Such action may be due initially to the presence of open-chain molecules augmented subsequently by hydrolysis, or it may be due to the hydrolysis alone.

The inulin of commerce, derived from dahlia tubers, contains a considerable amount of ash consisting of mineral bases and salts, part of which is soluble in water after ignition, yielding an alkaline solution. The main bulk of this mineral matter may be separated from the inulin by the following simple process: The inulin is dissolved rapidly in hot water, and the solution boiled for a few minutes with a little active charcoal which has been carefully freed from soluble salts; it is then filtered, and the process is repeated unless the filtrate is colourless and water-clear. The bulk of the inulin is then frozen out, redissolved, boiled momentarily with a little more charcoal, again frozen out, then redissolved and precipitated by a large excess of alcohol, washed with alcohol, and dried. The white powder obtained has no reducing action on

Fehling's solution during 24 hours in the cold, but shows sligl reduction on boiling or even on keeping at 50°. It contains abo 1 part in 1000 parts of ash, as determined by heating in a platinu boat with or without sulphuric acid (*e.g.*, 14·139 mg. gave 0·014 m of ash). The ash appears to consist mainly of silica. The wate content was determined by heating during $2\frac{3}{4}$ hours at 75° to 110° in stream of dry air at low pressure; the loss of water was 10% of th original weight of the sample (*e.g.*, 5·571 mg. lost 0·553 mg. of water) The resulting powder, which was extremely hygroscopic, gave o analysis: C, 44·3; H, 6·5 [$(C_6H_{10}O_5)_x$ requires C, 44·4; H, 6·2%]

The determination of the molecular weight, or average molecula weight, of "ash-free" inulin in boiling water was now attempted The initial assumption was necessarily made that inulin is unalterec in molecular structure by solution in boiling water. That an alteration, at least in physical structure, does occur, however, is evident from the abrupt change in the solubility of inulin in water between 80° and 100°: 100 c.c. of solution at 14° contain 0·02 g. of inulin; at 80°, 4·0 g.; and at 100°, no less than 36·5 g. This view receives some support, also, from our own observation that the position of the decomposition range on the temperature scale varies markedly with the amount of water retained by different samples of inulin; *e.g.*, the decomposition range is situated above 200° for specimens of "glassy" inulin rich in water, but is much lower for drier powdery samples. Inulin, as would be expected, never shows a true melting point. The molecular state of inulin in boiling water would nevertheless be of interest, and it is unfortunate that another complication enters into the determination. The apparent molecular weight of inulin in boiling water shows continuous diminution over a considerable period of time, and we have found that the reducing power of the solution rises as the molecular weight decreases, and that the action is not completely, if at all, reversed in the cold. These facts point distinctly towards the occurrence of hydrolysis.

The hydrolysis probably depends upon the presence of minute traces of acid electrolytes, since pellets made from the same bulk sample of inulin on different occasions did not always show the same initial molecular weights nor the same rate of hydrolysis, and pellets which had been handled with the fingers seemed to hydrolyse relatively rapidly. Contamination by the surface of the pellet-press was difficult to avoid and may partly account for the discrepancies. The following are typical examples of the results, *W* indicating the weight of water, *w* that of the water-free inulin, and the times being reckoned from that of the addition of the inulin (the pellets were seen to dissolve completely in from 1 to 2 minutes):

I.			II.			III.		
W, 14·7 g.; w, 0·8748 g.			W, 14·95 g.; w, 1·0701 g.			W, 14·35 g.; w, 1·2542 g.		
Mins.	Rise of b. p.	M.	Mins.	Rise of b. p.	M.	Mins.	Rise of b. p.	M.
3	0·008°	3870	5	0·012°	3100	4	0·011°	4130
7	0·011	2810	8	0·013	2860	7	0·014	3250
10	0·017	1820	23	0·020	1860	13	0·017	2670
17	0·024	1290	48	0·025	1490	28	0·022	2070
						39	0·025	1820

The times of observation were extended, in some cases, beyond hose shown, and it was found that the molecular weight continued o fall, even below 900. It is evident that no exact significance ıttaches to the figures, nevertheless they appear to us to indicate hat the initial molecular weight of inulin in boiling water is not ess than 3200 or 3600; *i.e.*, the inulin molecule contains not fewer han 20 or 24 anhydrofructose units. Initial experiments showed hat a perfectly steady indication of the boiling point of the water ;ould be obtained by placing clean fragments of garnets, mixed vith pieces of platinum foil, in the boiling-bulb (provided with a hick piece of platinum wire sealed into the lower extremity), so hat the height of the column of garnets, which terminated just below the bulb of the thermometer, bore a certain ratio to that of he column of water above it. Four minutes were allowed for the e-attainment of the true boiling point after the addition of the pellets, this time having been determined roughly by other measurements with the apparatus.

It will be clear that the molecular weight of inulin may be much higher than that indicated by these experiments, both because the initial changes of temperature are necessarily very small and because the initial effect of traces of electrolytes may be relatively very great. We hope to investigate this aspect of the matter in further experiments.

It seems clear that the results of Pringsheim and his co-workers (*loc. cit.*) can have little significance, unless he has succeeded in obtaining a specimen of inulin that is stable to boiling water. In any case, his procedure for the cryoscopic determination of the molecular weight (namely, to make up a solution of inulin in boiling water and then to cool it and determine the freezing point) is inadmissible, and the agreement of his cryoscopic and ebullioscopic results is possibly fortuitous.

It has frequently been stated that inulin shows, on hydrolysis by mineral acids, no intermediate stage between itself and fructose. Certain observations which we have made during the past two years indicate that this view is erroneous; and although our experiments have not resulted in the isolation of demonstrably homogeneous

intermediates, it seems desirable at this stage briefly to indi(their nature.

When a stream of carbon dioxide is passed during about 2 d: through an aqueous solution of inulin, the solution being occasiona warmed to redissolve any inulin which has separated, a considera proportion of the inulin becomes changed to a white powder havi a lower range of decomposition on heating than inulin and shows tendency to effervesce at higher temperatures. The powder diff from inulin, also, in that it is readily soluble in cold water to a wat clear solution which does not foam when shaken. The product, t specific rotation of which in water is rather higher than that shov by inulin, has a greater reducing action towards hot Fehling solution.

The same effect can be produced by treating an aqueous soluti of inulin in an autoclave with carbon dioxide at a pressure of abo 230 lb./sq. in. during about 24 hours. Unchanged inulin is filtere off, and the clear solution is precipitated by the addition of a excess of acetone, a product similar to the foregoing being obtaine(

The transformation may also be brought about in the dry wa at the ordinary temperature. For instance, when inulin powde is kept in a desiccator in which is present a little vaporous ethy chloroformate, the inulin is gradually changed into a produc similar to that already described. The change may take many months; its speed seems to depend upon the proportion of wate present in the inulin, very dry inulin requiring a longer period This behaviour indicates that the change is hydrolytic, and that it is produced by traces of hydrochloric acid generated by the decomposition of the chloroformate in the presence of water.

A sample of inulin powder which has become "infected" in this manner suffers progressive degradation even when the chloroformate vapour is removed; and, if the infection be acute or if the water content of the original inulin be high, the powder may finally change to a yellow syrup which contains much fructose. Inulin may be "infected" without the agency of chlorinated substances; *e.g.*, inulin which has been recovered by precipitation with acetone from aqueous solutions treated with carbon dioxide undergoes the change when kept in a desiccator over phosphoric oxide or calcium chloride. In such cases the change is slow and the final product is a flaky powder apparently free from ordinary fructose.

The change may in most cases be arrested by repeatedly dissolving the sample in water and reprecipitating it by means of acetone. In some cases, however, even this treatment does not prevent the occurrence of slow subsequent change.

Naturally, the method of isolation by precipitation leads to

fractionation of the product, the more soluble products of lower molecular weight remaining in solution. Our attention has been mainly directed towards the water-soluble product (precipitable by acetone) which can usually be obtained in high yield.

We have not succeeded in showing that this product is molecularly homogeneous, but we believe that it approximates to this condition and that it is an open-chain compound, of high molecular weight, containing one or two free reducing groups in the molecule. The following is a description of the product, which may be regarded as analogous to a starch dextrin.

Inulin "lævulin." The substance obtained in the foregoing manner was carefully separated from unchanged inulin and from substances of lower molecular weight by repeated solution in cold water, filtration, and reprecipitation with acetone. The fine white powder so obtained (7 g.) dissolved to a slightly opalescent solution in 75 c.c. of water at 19° ; the solution was passed through a stream-line filter, which was rinsed with a further 125 c.c. of water. The clear, colourless solution, neutral to litmus and quite free from halogen and methoxyl, was now treated slowly with 300 c.c. of acetone. After 1½ hours, the white, granular precipitate (5 g.) was collected, washed with 100 c.c. of acetone, and kept over phosphoric oxide. The substance melted to a white, opaque paste at about 142°, and the paste became a white froth near 185°. It was dehydrated in a vacuum during 11 hours at 80°, then during 24 hours at 95°, and finally at 120° during 6 hours, the loss of water amounting to about 7·5% (Found : C, 43·8 ; H, 6·5%). The product contained 1% of ash, which was allowed for in the analysis. A sample dried at 90° in a vacuum had $[\alpha]^{21°}_{5461}$ −45·8° in water ($c = 4·778$) and showed no mutarotation after a month. Other samples showed approximately the same rotation.

Cryoscopic determinations of the molecular weight in water gave results varying between 900 and 1100 for the undried material, and between 1200 and 1600 for the material dried at 90° in a vacuum. Ebullioscopic determinations gave results varying between 1400 and 1800.

It is doubtful whether much significance can be attached to these figures; but it seems possible that the effect of dehydration or of hot water tends to change the product back in the direction of inulin by the relinking of chains opened in the former degradation process.

Another sample of this product, prepared in a similar way, was ash-free, lost 7% of water when dried in a vacuum at 80° during 8 hours, melted to a white paste at about 145° and frothed at a higher temperature (Found : C, 43·5 ; H, 6·5%). Many other

analyses were carried out on similar products dried under vario conditions, the average of these results showing *C*, 43·3; H, 6 (octasaccharide requires C, 43·8; H, 6·2%; *M*, 1314. Hexa saccharide requires C, 43·6; H, 6·3%; *M*, 990). The substanc reduces dilute Fehling's solution at 50°, the reduction commencin after a few minutes and being considerable in 10 minutes, wherea inulin under these conditions showed only a trace of reducing actio after ½ hour.

Experience has shown that it is important to remove the ash a completely as possible from inulin before investigating the propertie of this substance, a consideration which we did not at first closel regard. We intend to repeat our experiments with ash-free inulir if this is attainable. It is possible that inulin is protected from th hydrolysing action of boiling water by the presence of weakl alkaline mineral matter contained among the "ash," and that the removal of ash, either by purification or by neutralisation with traces of acid, permits the onset and continuation of the hydrolysing process which we have described; but it is not yet certain that the hydrolysis of inulin by boiling water is a process identical with the catalytic degradation taking place in the dry way.

By allowing the transformation of inulin to proceed to different lengths, products of lower decomposition range have been isolated. These are considered to be mixtures of compounds containing shorter chains. The best-defined was a *substance* obtained, by the action of carbon dioxide on aqueous inulin, as a white powder which melted to an opaque paste at 85—86° and effervesced at 120—125°. This was readily soluble in cold water and had $[\alpha]^{20°}_{5461}$ $-45·6°$ in water ($c = 2·28$), the negative rotation slightly increasing with time. A further specimen, of initial m. p. 92—95°, gave C, 42·0; H, 6·8%; *M* (cryoscopic), 520 in water. The substance may be an impure tetra- or tri-saccharide in a partly hydrated condition. It reduced warm Fehling's solution, and also cold aqueous potassium permanganate on standing.

Summary.

It is considered probable that inulin consists of chains of fructofuranose or γ-fructose rings, the molecule containing at least 20 or 24 such rings.

Degradation, by means of carbon dioxide or a trace of hydrogen chloride, consists in the hydrolytic scission of the chains at junctions between the rings, polysaccharides with shorter chains being produced. Dehydration may in certain circumstances tend to regenerate the longer-chain polysaccharides or inulin itself. Complete scission probably leads to the production of γ-fructose, which is

then irreversibly changed to ordinary fructose. The migration of inulin in plant stems may possibly occur through the formation of water-soluble polysaccharides which are subsequently dehydrated to inulin in the tubers.

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CCCLVI.—*A Contribution to the Chemistry of Nitroso-compounds.*

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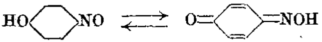
THE remarkable ease with which nitroso-compounds are reduced to hydroxylamino-derivatives by cold dilute hydriodic acid at the ordinary temperature (Earl and Kenner, J., 1927, 2139) has led us to consider the reaction more closely. It is well known that nitroso-chlorides, if not polymerised, are usually oximes, and even in those cases in which a polymeride of the true nitrosochloride is known, *e.g.*, pinol nitrosochloride, it can be changed into the *iso*nitroso-modification. Further, no indication has been found that the reaction is reversible, and, in the case of the oximes themselves, it is only comparatively recently that any evidence of a reversion to the nitroso-form has been obtained (Griffiths and Ingold, J., 1925, **127**, 1698). It is true that the tautomerism of *p*-nitrosophenol involves such a reversal, but this is due to the general inclination of quinonoid compounds to assume the more saturated benzenoid condition :



In these cases the change to the oximino-form is intramolecular, but the same tendency appears in intermolecular reactions. The facility with which *p*-nitrosodimethylaniline is converted into *p*-nitrosophenol by hydrolysis is perhaps the most familiar instance of this kind, and the reduction of nitroso-compounds to hydroxyl-amines by hydriodic acid is a reaction governed by the same tendency. In our view, it is best formulated as an additive reaction in the first place, followed by displacement of the iodine atom by

The formation of *N*-hydroxyamidines from nitrosobenzene and methyleneanilines (Burkhardt, Lapworth, and Robinson, J., 1925, **127**, 2234) is also to be included under this heading :

$$Ar{\cdot}N{:}O + Ar'{\cdot}N{:}CH_2 \longrightarrow Ar{\cdot}N(OH){\cdot}CH{:}NAr'.$$

This brief review throws new light on the classical synthesis of glycerol by Piloty and Ruff (*Ber.*, 1897, **30**, 1656). This depends on the elimination of formaldehyde, which occurs when the hydroxylaminobutanetriol (I) is subjected to oxidation by yellow mercuric oxide. Clearly the reaction is only another illustration of the property of the nitroso-group just discussed :

$$\underset{\text{(I.)}}{(CH_2{\cdot}OH)_3C{\cdot}NH{\cdot}OH} \longrightarrow [(CH_2{\cdot}OH)_3C{\cdot}NO] \longrightarrow CH_2O + (CH_2{\cdot}OH)_2C{:}NOH.$$

The corresponding nitrobutanetriol (II) is itself stable, but also loses formaldehyde under the influence of alkali (Schmidt and Wilkendorf, *Ber.*, 1919, **52**, 389). Wilkendorf and Trénel (*Ber.*, 1923, **56**, 611) were, however, unable to accomplish the direct elimination of a second molecule of formaldehyde from the nitrobutanetriol. But the foregoing considerations make it clear that this must occur if a nitroso-group be appropriately introduced into the molecule of β-nitropropane-αγ-diol (III).

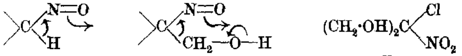
$$\text{(II.)}\ (CH_2{\cdot}OH)_3C{\cdot}NO_2 \longrightarrow CH_2O + (CH_2{\cdot}OH)_2C{:}NO_2H\ \text{(III.)} \longrightarrow$$
$$\text{(IV.)}\ [(CH_2{\cdot}OH)_2C(NO_2){\cdot}NO] \longrightarrow HO{\cdot}CH_2{\cdot}C(NO_2){:}NOH\ \text{(V.)}$$
$$\uparrow$$
$$HO{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2\ \text{(VI.)}$$

This prediction has been experimentally verified by treatment of the sodium salt of the diol with nitrous acid under precisely those conditions prescribed by V. Meyer and Constam (*Annalen*, 1882, **214**, 328) for the preparation of ethylnitrolic acid from nitroethane. The action of nitrous acid on the cooled aqueous solution of the salt at first causes the production of the characteristic well-known blue colour indicative of the formation of the pseudonitrol (IV), but this almost at once gives place in the alkaline solution to the red colour of the nitrolic acid salt. The formaldehyde produced has been identified by its condensation with β-naphthol, and the β-*hydroxyethylnitrolic acid* (V) has been isolated in the crystalline condition, and its constitution also established by its identity with the product obtained in the usual manner from β-nitroethyl alcohol (VI). Since, however, the sodium salt of β-nitropropane-αγ-diol is obtainable in one operation from nitromethane and formaldehyde (Wilkendorf and Trénel, *loc. cit.*), whereas nitroethyl alcohol has to be prepared from glycolchlorohydrin through the

iodohydrin and, as we found, then requires further purification through its sodium salt for the present purpose, the new reaction is the more convenient method of obtaining the acid. In order to demonstrate the general character of the reaction, we have also shown that ethylnitrolic acid is produced by the action of nitrous acid on the sodium salt of β-nitropropanol:

$$CH_3{\cdot}C(CH_2{\cdot}OH){:}NO_2Na \longrightarrow CH_3{\cdot}C(NO_2){:}NOH + CH_2O.$$

These reactions indicate that when the carbon atom next the nitroso-group does not carry a hydrogen atom which would enable *the change, indicated in (VII), to the oximino-condition to occur,*



(VII.) (VIII.) (IX.)

a methylol group can supply the necessary hydrogen atom, as shown by (VIII). In this case the electronic changes induced by the nitroso-group are transmitted through a chain of singly linked atoms. The same applies to the case of the nitrobutanetriol (II) and the fact that β-chloro-β-nitropropane-αγ-diol (IX) suffers elimination of formaldehyde rather than elimination of chlorine (Wilkendorf and Trénel, *loc. cit.*) illustrates the readiness with which such transmission occurs.

A number of other well-known reactions appear to depend on *the characteristic of the nitroso-group emphasised above.* For instance, the exceptional behaviour of nitrous acid in so readily forming an anhydride can be ascribed to the following reactions:

$$HO{\cdot}N{:}O + H{\cdot}ON{:}O \longrightarrow HO{\cdot}N{<}^{OH}_{ON:O} \longrightarrow H_2O + O{:}N{\cdot}O{\cdot}N{:}O.$$

Similarly, the almost instantaneous esterification of ethyl alcohol by cold dilute nitrous acid (compare Thiele and Eichwede, *Annalen*, 1900, **311**, 366, footnote) and the course of the well-known reactions between potassium nitrite and potassium hydrogen sulphite (Raschig, *Annalen*, 1887, **241**, 207) are readily understood from this point of view. Again, the interaction of hydriodic acid and nitrous acid would, according to the scheme already suggested for nitroso-compounds in general, lead to the compound (X), which could then

$$\underset{(X.)}{HO{\cdot}NH{\cdot}OH} + HO{\cdot}N{:}O \longrightarrow HO{\cdot}N(OH){\cdot}N(OH)_2 \longrightarrow 2H_2O + \underset{\displaystyle \downarrow \atop \displaystyle 2NO.}{O{:}N{\cdot}N{:}O}$$

react with more nitrous acid in the manner indicated, resulting in the eventual formation of nitric oxide.

Again, nitrous acid probably derives its distinctive value as a reagent for reactive methylene groups from its tendency to form an oximino-derivative (compare Wolff, *Annalen*, 1895, **288**, 10):

$$-\overset{|}{C}H_2 \longrightarrow -\overset{|}{C}H{\cdot}N(OH)_2 \longrightarrow -\overset{|}{C}{:}NOH + H_2O.$$

It does not seem previously to have been realised that, owing to the correspondence in chemical relationships of the CH group with the nitrogen atom and of the imino-group with the oxygen atom, a close constitutional connexion exists between methyl alcohol, hydroxylamine, and hydrogen peroxide, and, in fact, each undergoes catalytic dehydrogenation by platinum-black. Extending now Wieland's formulation in the cases of methyl alcohol and hydrogen peroxide (*Ber.*, 1921, **54**, 2353) to that of hydroxylamine, we have:

$$H{\cdot}N{<}^{H}_{OH} \longrightarrow H_2 + HN{:}O.$$

Actually ammonia, water, and nitrous oxide are formed (Tanatar, *Z. physikal. Chem.*, 1902, **40**, 475). Apparently nascent hydrogen and a part of the "nitroxyl" first formed give rise to ammonia, whilst the remainder is converted into nitrous oxide:

$$2HNO \longrightarrow HN(OH){\cdot}N{:}O \longrightarrow N{\vdots}N{:}O.$$

This gas is produced quantitatively by oxidation of hydroxylamine with ferric sulphate (Raschig, *Annalen*, 1887, **241**, 188; *Z. anorg. Chem.*, 1904, **17**, 1411) as well as by reduction of nitrous acid (Raschig, *Z. anorg. Chem.*, 1904, **17**, 1398) and, particularly interesting for the present discussion, by hydrolysis of nitrososulphonic acid (compare Abegg, "Handbuch der Anorganischen Chemie," 3, ii, 153):

$$O{:}N{\cdot}SO_3H + H_2O \longrightarrow H_2SO_4 + HN{:}O.$$

In the previous paper (Earl and Kenner, *loc. cit.*) it was pointed out that in spite of the well-recognised analogy between the carbonyl and the nitroso-group, the former does not undergo reduction with cold dilute hydriodic acid. This corresponds with the greater stability of the ketonic than the enolic form of simple carbonyl compounds, and the foregoing considerations would therefore lead

(XI.) $>C{<}^{CH_2{\cdot}OH}_{CHO}$ $(CH_2{\cdot}OH)_3C{\cdot}CHO$ (XII.)

(XIII.) $CH_3{\cdot}C(CH_2{\cdot}OH)_2{\cdot}CHO$ $CHMe_2{\cdot}C(CH_2{\cdot}OH)_2{\cdot}CHO$ (XIV.)

us to anticipate that the grouping (XI) would be stable and not lose formaldehyde under ordinary conditions. Accordingly penta-

erythrose (XII) (McLeod, *Amer. Chem. J.*, 1907, **37**, 20), αα-dimethylolpropanal (XIII) (Koch and Zerner, *Monatsh.*, 1901, **22**, 448), and αα-dimethylol-β-methylbutanal (XIV) (Lichtenstern, *ibid.*, 1905, **26**, 499) have been described and satisfactorily identified. On the other hand, Rave and Tollens showed that when pentaerythritol is oxidised by dilute nitric acid one of the products is an *aldehyde of the empirical formula* $C_4H_6O_3$, *to which they assigned the constitution* $CHO{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CHO$ (*Annalen*, 1893, **276**, 65). In our view, the present discussion makes it practically certain that the course of the reaction is to be represented as follows:

$$(CH_2{\cdot}OH)_4C \longrightarrow (CH_2{\cdot}OH)_2C{<}{}^{CHO}_{CHO} \longrightarrow CH_2O + HO{\cdot}CH_2{\cdot}C{<}{}^{CHO}_{CH{\cdot}OH}$$

But our preliminary experiments to verify this hypothesis have shown that the task of preparing the dialdehyde in any quantity is likely to be laborious, since our yield of the characteristic bisphenylhydrazone described by Rave and Tollens was exceedingly small.

The difference between the nitroso- and the carbonyl group illustrated by these various reactions is one of degree, and is attributable to the fact that the nitrogen atom is more nearly equal to the oxygen atom than is the carbon atom in its tendency to acquire electrons. A system, therefore, in which nitrogen and oxygen atoms compete for four electrons is less likely to be stable than a similar one in which carbon occupies the place of nitrogen.

EXPERIMENTAL.

The solutions of sodium nitrite and potassium hydroxide employed in the following experiments contained respectively 64 g. and 53·6 g. in 120 c.c., as recommended by Meyer and Constam (*loc. cit.*).

β-*Hydroxyethylnitrolic Acid* (V).—Demuth and V. Meyer (*Annalen*, 1890, **256**, 43) were unable to obtain this compound either from β-nitroethyl alcohol or from the sodium salt, the preparation of which serves as a means of purifying the alcohol obtained by the usual method from glycoliodohydrin. Although the nitroethyl alcohol employed in our work was carefully purified by distillation at 101°/15 mm. (corr.) (compare Henry, *Rec. trav. chim.*, 1898, **17**, 2), we also were unable to isolate the nitrolic acid in experiments conducted under exactly the same conditions (the amount of alkali used was, however, three times as great in order to convert the nitro-compound into its salt) as those applied to the sodium salt in the manner now to be described.

β-Nitroethyl alcohol (13 g.) was converted into its sodium salt by treatment with a solution of sodium (3·3 g.) in alcohol (90 c.c.).

A solution of the sodium salt (11·4 g.) in water (5 c.c.), aqueous sodium nitrite (17 c.c.), and potassium hydroxide solution (5·6 c.c.), having been gradually acidified between $-10°$ and $0°$ with dilute sulphuric acid (5*N*), was again rendered alkaline and, after a few moments, re-acidified (compare Meyer and Constam, *loc. cit.*; Wieland, *Annalen*, 1907, **353**, 82). The solution was then rapidly filtered from sodium sulphate and extracted three times with cooled purified ether. Finally, the extract (40 c.c.), having been washed in a little ice-water and dried over sodium sulphate, was evaporated in a vacuum desiccator, first over sulphuric acid and then over phosphoric oxide. Crystallisation set in after 1 hour, when almost the whole of the ether had been removed, and the pure *nitrolic acid* (4 g.), m. p. 76—77° (decomp.; corr.), was obtained (Found: N, 23·2. $C_2H_4O_4N_2$ requires N, 23·3%). The poor yield (33%) was due to the solubility of the acid in water and to the undesirability of increasing the volume of ethereal extract and consequently delaying isolation of the product. It could be crystallised from solution in the minimum volume of dry ether by addition of three volumes of light petroleum, but gradually decomposed with evolution of nitrous fumes, even in a vacuum desiccator.

When an exactly similar experiment was performed with an equimolecular proportion of the sodium salt of β-nitropropane-αγ-diol (Wilkendorf and Trénel, *loc. cit.*) each addition of sulphuric acid was followed by the appearance of a temporary blue coloration, which rapidly changed to red. The product, m. p. 76—77° (decomp.) (Found: N, 22·9, 23·2%), did not depress the melting point of the specimen of β-hydroxyethylnitrolic acid obtained from β-nitroethyl alcohol. In order satisfactorily to demonstrate the production of formaldehyde in the reaction, it was necessary to examine the aqueous liquors under conditions which would avoid as far as possible decomposition of unextracted nitrolic acid into glycollic acid, and also to separate the formaldehyde from any of this acid which might nevertheless be produced. The liquors were therefore at once shaken with an excess of calcium carbonate at the ordinary temperature and the formaldehyde was removed by distillation after 24 hours. The distillate, which reduced Tollens's solution, was treated with β-naphthol in presence of hydrochloric acid, and furnished methylenedi-β-naphthol which, alone or mixed with an authentic specimen, melted at 206° (corr.).

Ethylnitrolic Acid from β-Nitropropanol.—A solution of sodium (5·7 g.) in methyl alcohol (40 c.c.) was very slowly added to a vigorously stirred solution of nitroethane (16 g.) and paraformaldehyde (6·6 g.) in methyl alcohol (120 c.c.). Owing to its solubility in methyl alcohol, the yield of the *sodium* salt of β-nitropropanol

(Found: N, 11·3; Na, 18·1.* $C_3H_6O_3NNa$ requires N, 11·0; Na, 18·1%) which separated from the solution was only 50%.

From the sodium salt (3·4 g.) and sodium nitrite (5 c.c.) and potassium hydroxide (1·7 c.c.) solutions, by the procedure already detailed in the case of nitroethyl alcohol, ethylnitrolic acid (2·7 g.), m. p. 84—85° (decomp.; corr.), was obtained. It was identified by analysis (Found: N, 26·6. Calc. for $C_2H_4O_3N_2$: N, 26·9%) and by direct comparison with a specimen, m. p. 85° (decomp.; corr.), prepared from nitroethane. The aqueous liquor from the preparation furnished a distillate in which formaldehyde was identified by condensation with β-naphthol; the methylenedi-β-naphthol obtained melted at 206° (corr.).

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CCCLVII.—*The 3-Halogeno-2-, -4-, and -6-aminophenols.*

By HERBERT HENRY HODGSON and ARNOLD KERSHAW.

THE compounds herein described include all the 3-halogeno-2-, -4-, and -6-aminophenols except the fluoro-compounds. They are much stabler than the unsubstituted aminophenols, remaining colourless after prolonged exposure to air and having no action on Fehling's solution. Ammoniacal silver nitrate, however, is reduced, rapidly by the 3-halogeno-6-aminophenols (order: Cl > Br > I), much more slowly by the 3-halogeno-2-aminophenols (I > Br > Cl), and relatively most slowly by the 3-halogeno-4-aminophenols (Cl > Br > I). The solubilities of the 3-halogenoaminophenols in water decrease in the order Cl > Br > I. The hydrochlorides of the 3-halogeno-2- and -6-aminophenols are very soluble in water; those of the 4-amino-isomerides are only moderately easily soluble.

EXPERIMENTAL.

General Method of Preparation.—The 3-halogeno-2-, -4-, and -6-nitrophenols are dissolved in hot aqueous sodium hydroxide, and solid sodium hyposulphite is gradually added. The resulting 3-halogenoaminophenols all crystallise from water containing a little sodium bisulphite, and their hydrochlorides from dilute

* The result of the nitrogen determination was only satisfactory when the salt was mixed with potassium dichromate (compare Schmidt and Wilkendorf, *loc. cit.*). For the sodium determination, the salt was moistened with water before treatment with sulphuric acid.

hydrochloric acid, in colourless needles or plates. The hydrochlorides melt with extensive decomposition.

The 3-Halogeno-2-aminophenols.—Colour reactions. (1) Ferric chloride produces a transient reddish-violet colour and then a brown precipitate, the solution of which in concentrated hydrochloric acid retains its deep brownish-red colour on dilution. (2) Bleaching powder solution produces a light brown precipitate which deepens in colour on the gradual addition of hydrochloric acid but finally dissolves, forming deep brown solutions from the chloro- and bromo-compounds and a yellow solution from the iodo-compound. (3) Bromine water gives initially a brown coloration and then a pale yellow precipitate, the solution of which in hydrochloric acid is yellow.

3-*Chloro-2-aminophenol*, flat needles, m. p. 122° (Found : Cl, 24·8. C_6H_6ONCl requires Cl, 24·7%); *hydrochloride*, plates (Found : Cl, 39·2. C_6H_6ONCl,HCl requires Cl, 39·4%). 3-*Bromo-2-aminophenol*, needles, m. p. 138° (Found : Br, 42·3. C_6H_6ONBr requires Br, 42·6%); *hydrochloride*, needles (0·0930 g. gave 0·1369 g. of mixed silver halides. Calc., 0·1372 g.). 3-*Iodo-2-aminophenol*, needles, m. p. 137° (decomp.) (Found : I, 54·2. C_6H_6ONI requires I, 54·0%); *hydrochloride*, plates (0·1597 g. gave 0·2228 g. of mixed silver halides. Calc., 0·2226 g.).

The 3-Halogeno-4-aminophenols.—Colour reactions. (1) Ferric chloride gives with the chloro- and bromo-compounds intense violet colours which are changed to greenish-brown by concentrated hydrochloric acid and restored on dilution, whereas the iodo-compound gives only a faint brown colour changing to orange-brown. (2) Bleaching powder solution produces with the chloro- and bromo-compounds purple colorations and then brown precipitates giving orange-brown solutions in hydrochloric acid, whereas the iodo-compound exhibits only a faint violet coloration changing to light yellow on acidification. (3) Bromine water produces initially a violet colour, followed by a light brown or buff precipitate soluble in hydrochloric acid to a golden-brown solution.

3-Chloro-4-aminophenol, long, flat needles, m. p. 159·5° (Found : Cl, 24·5%) (compare D.R.-P. 143449, 1903); *hydrochloride*, plates (Found : Cl, 39·2%). 3-*Bromo-4-aminophenol*, very long needles, m. p. 151° (Found : Br, 42·6%); *hydrochloride*, prisms (0·2221 g. gave 0·3285 g. of mixed silver halides. Calc., 0·3278 g.). 3-*Iodo-4-aminophenol*, plates, m. p. 145·5° (Found : I, 53·8%); *hydrochloride*, plates (0·1180 g. gave 0·1650 g. of mixed silver halides. Calc., 0·1645 g.).

The 3-Halogeno-6-aminophenols.—Colour reactions. (1) Ferric chloride gives initially a bright violet colour, followed by a dark

purple precipitate the reddish-brown solution of which in concentrated hydrochloric acid becomes violet on dilution. (2) Bleaching powder solution produces a transient violet coloration, followed by a deep brown precipitate which rapidly changes to a bright red gelatinous form soluble in hydrochloric acid to an eosin-red solution unchanged on dilution. (3) Bromine water gives initially a brown coloration, followed by a light brown precipitate soluble with difficulty in hydrochloric acid to a straw-coloured solution.

3-Chloro-6-aminophenol, prisms, m. p. 154° (Found : Cl, 24·5%); *hydrochloride*, plates (Found : Cl, 39·3%). *3-Bromo-6-aminophenol*, prisms, m. p. 150° (Found : Br, 42·4%); *hydrochloride*, elongated plates (0·1137 g. gave 0·1699 g. of mixed silver halides. Calc., 0·1678 g.). *3-Iodo-6-aminophenol*, long needles, m. p. 141° (Found : I, 54·2%); *hydrochloride*, plates (0·1234 g. gave 0·1727 g. of mixed silver halides. Calc., 0·1720 g.).

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HUDDERSFIELD. [*Received, July 13th*, 1928.]

CCCLVIII.—*Adsorption and Constitution: The Adsorption of Organic Acids on Animal Charcoal.*

By KENNETH MASSY GRIFFIN, HENRY LORIMER RICHARDSON, and PHILIP WILFRID ROBERTSON.

IT has been shown that the expression C_2/C_1 gives a comparable measure of the adsorption of substances from solution (Richardson and Robertson, J., 1925, **127**, 553), *i.e.*, the order of the values of C_2/C_1 found for a number of compounds agreed with the relative position of their adsorption isotherms, the effect of initial concentration being limited to that due to differences in the slope of the isotherms. Further, the magnitude of C_2/C_1 varied over a wide range with changes in the structure of the substances compared.

The equilibrium of an adsorbed substance in contact with its solution—the adsorption isotherm—is generally expressed by the exponential formula of Freundlich, $a = \alpha c^{1/n}$, or $C_2 = KC_1^{1/n}$, which gives satisfactory results at least for dilute solutions. An examination of the values of $1/n$ for a number of widely diverse substances (Freundlich, "Kapillarchemie," 1923, 236) showed very little dependence on the nature of the molecule adsorbed; a lay

between 1·8 and 4·2. Richardson and Robertson (*loc. cit.*) made a similar observation with a variety of organic compounds. Apart from the ambiguity of its actual significance, therefore, and the experimental difficulties of its determination in solvents where adsorption is slight, n does not seem to be a suitable function for the examination of constitutive influences.

The relative extent to which substances are adsorbed varies much more considerably than does n : some comparative studies on this basis, of the adsorption of organic acids from aqueous solution, have been reported (Freundlich, *op. cit.*, p. 267; Bartell and Miller, *J. Amer. Chem. Soc.*, 1923, **45**, 1109). However, for a more general examination of organic compounds, owing to their slight solubility in water, organic solvents would be necessary. In the present paper, the adsorption by animal charcoal from ethyl-alcoholic solution of a number of carboxylic acids has been determined. The concentration chosen as a basis of comparison was $N/20$: C_2/C_1 was calculated from this after titration of the equilibrium filtrate, and then the "relative adsorption" with reference to a standard acid (acetic for the aliphatic series, benzoic for the aromatic) was taken for comparison. This "relative adsorption" was found to be almost independent of the activity of the charcoal.

EXPERIMENTAL.

The method of experiment was as described in the literature : 1 g. of charcoal were shaken mechanically for 4 hours with 50 c.c. of an $N/20$-alcoholic solution of the acid, the liquid was rapidly filtered, and 10 c.c. portions of the filtrate were titrated with $N/20$-alcoholic potash with phenolphthalein as indicator. The original solution was titrated at the same time as the filtrate from the charcoal, to allow for error due to esterification. Only those titration values that differed by less than 0·1 c.c. were accepted; agreement was generally within 0·05 c.c.

The reagents used were carefully purified. The animal charcoal was supplied by the British Drug Houses as "Animal Charcoal, Acid-free," and since it had at first a slightly alkaline reaction, it was repeatedly extracted with hot water until neutral to phenolphthalein. Before use, it was activated by heating to redness for some hours in a Vitreosil tube, a steady stream of dry nitrogen being passed through towards the end of the operation and continued until the tube was cold. After being sieved, the charcoal was kept in a large, stoppered bottle for several days before use, for its activity fell off somewhat immediately after activation. Since the amount of charcoal used in a series of experiments was considerable, it became necessary to recover it after use and reactivate it : this was

effected in the same manner as the preliminary activation. After reactivation, the activity of the charcoal as measured by a standard substance such as acetic acid was found to have changed slightly: in one series of reactivations, C_2/C_1 for acetic acid was successively 1·35, 1·19, 0·98, 1·10, 0·75; another charcoal gave 0·36, 0·46, 0·43, 0·33, 0·39. To enable comparable results to be obtained with charcoals of different activity, the values of C_2/C_1 found for a series of compounds with any one charcoal were divided by the previously determined value of C_2/C_1 for a standard acid with that charcoal. As noted above, these "relative adsorptions" obtained for any compound with different charcoals were in satisfactory agreement, but in certain instances the deviations were greater than the experimental error. It would appear that when the structure of the compounds differed considerably, the relative adsorption might be influenced to some extent by the nature of the charcoal. This is shown by observations on acetic and benzoic acids:

Charcoal.	C_2/C_1, acetic acid.	C_2/C_1, benzoic acid.	Relative adsorption (acetic acid = 1).
I	0·362	1·67	4·61
II	0·463	2·24	4·84
III	0·433	2·48	5·73
IV	0·330	2·08	6·32
V	0·387	2·59	6·69
VI	0·067	0·339	5·1

Charcoals II, III, IV, and V were obtained by successive reactivations of charcoal I; reactivation caused a slight but steady increase in the relative adsorption of benzoic acid as compared with acetic acid. Charcoal VI was a sample of different origin, and considerably less active; the value it gave for the relative adsorption of benzoic acid fell amongst those of the previous charcoals. The other aromatic acids resembled benzoic acid in showing appreciable deviations among their relative adsorptions with different charcoals, when the value for acetic acid was taken as unity. For this reason, the values for their relative adsorptions that appear in Table II were calculated on the basis of benzoic acid; the results so obtained showed satisfactory agreement for different samples of charcoal.

In Tables I and II are given the mean values found for the relative adsorptions from alcoholic solution of aliphatic and aromatic acids, respectively. For the former, acetic acid was taken as standard; for the latter, benzoic.

The effect of constitution is on the whole definite. In the normal fatty acids, the adsorption falls to a minimum and then rises with increasing molecular weight; further, the property is an alternating one, the odd-numbered members being less adsorbed than the even.

TABLE I.

Acid.	Relative adsorption.	Acid.	Relative adsorption.
Acetic	1·00	Lactic	0·58
Propionic	0·65	Phenylacetic	3·26
Butyric	0·87	Phenylpropionic	4·04
*iso*Butyric	0·27	Cinnamic	6·25
*iso*Valeric	0·21	Mandelic	2·29
Hexoic	1·13	Succinic	1·44
Heptoic	0·92	Adipic	1·05
Octoic	1·50	Sebacic	2·30
Nonoic	1·32	Monobromosuccinic	1·77
Lauric	2·15	Ethylsuccinic	0·85
Stearic	2·32	Malic	1·22
Monochloroacetic	2·31	Tartaric	1·60
Trichloroacetic	0·27	Fumaric	4·15
Monobromoacetic	2·70	Citraconic	5·54
α-Bromopropionic	1·92	Mesaconic	3·41
α-Bromo*iso*butyric	1·38		

With regard to the effect of substituents, small alkyl groups and the hydroxyl group reduce the adsorption, and halogen (except in trichloroacetic acid) and the phenyl group increase it. Dibasic acids are adsorbed more strongly than the corresponding monobasic acids. Unsaturation (the ethylenic link) causes an especially marked increase in relative adsorption.

TABLE II.

Acid.	Relative adsorption.	Acid.	Relative adsorption.
Benzoic	1·00	*p*-Nitrobenzoic	3·64
o-Toluic	0·97	*o*-Chlorobenzoic	0·86
m-Toluic	1·19	Salicylic	1·64
p-Toluic	1·36	*o*-Acetoxybenzoic	0·75
o-Bromobenzoic	1·01	*p*-Methoxybenzoic	2·30
m-Bromobenzoic	2·10	Phthalic	2·30
p-Bromobenzoic	2·42	*o*-Aminobenzoic	2·91
o-Nitrobenzoic	1·34	*o*-Acetamidobenzoic	2·30
m-Nitrobenzoic	3·32	*s*-Tribromobenzoic	2·51

Generally the relative adsorption of the aromatic acids is 5 to 20 times that of the aliphatic acids (compare table, p. 2707). Substituents in the para-position increase the relative adsorption, the effect of the groups being in the order alkyl, halogen, nitro-; in the meta-position there is a corresponding but smaller enhancement; and ortho-substitution has usually a smaller or even a depressing effect. The enhancement attributable to *o*-hydroxy- and *o*-amino-groups was reduced by acetylation. As in the aliphatic series, the additional carboxyl group of a dibasic acid increased adsorption.

Summary.

1. The relative adsorption of organic acids from alcoholic solution, on animal charcoal, varies within wide limits; *e.g.*, *iso*valeric acid

has the value 0·21, and *p*-nitrobenzoic acid 17, if acetic acid is taken as unity.

2. In general, the relative adsorption tends to increase with molecular weight, but this increase is subject to marked constitutive effects.

3. Aromatic acids are much more strongly adsorbed than aliphatic acids; substitution, especially in the para-position, increases the adsorption.

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CCCLIX.—*Polymerides of Aliphatic Chloroaldehydes.*

By FREDERICK DANIEL CHATTAWAY and EDWIN GEOFFREY KELLETT.

THE known polymerides of the aliphatic chloroaldehydes may be grouped in two classes, the so-called meta- and para-aldehydes. The meta-compounds are insoluble, colourless, amorphous solids, which on heating volatilise and dissociate without previously melting; they have no properties which afford a guide to their constitution, since in all reactions they revert to and react as the unpolymerised forms, and their molecular complexity is unknown. Metachloroacetaldehyde (Natterer, *Monatsh.*, 1882, **3**, 447) and metadichloroacetaldehyde (Friedrich, *Annalen*, 1881, **206**, 52) are readily formed from the free aldehydes under the influence of hydrogen chloride, whilst strong sulphuric acid causes the formation of polymerides of a different type—the para-aldehydes (Natterer, *loc. cit.*; Jacobsen, *Ber.*, 1875, **8**, 88). These are colourless, crystalline solids having sharp melting points, and being soluble in most organic solvents, though insoluble in water. They are comparatively stable, being unaffected by, *e.g.*, boiling aqueous alkalis. On distillation under ordinary pressure they dissociate, but under diminished pressure they volatilise unchanged. They are trimeric, and their constitution is usually represented by a six-atom ring.

Although chloral has long been known to give a polymeride of the meta-type, it has not hitherto been found to give one of the para-type. When, however, a solution of chloral in strong sulphuric acid is allowed to remain at the ordinary temperature, two isomeric *parachlorals* are formed in addition to the metachloral which is the main product, and they may be extracted from the latter by hot alcohol. By fractional crystallisation from the same solvent, they can be separated from each other and from chloralide

extent at the same time and is considerably less soluble than either. The production of these polymerides appears to depend on the temperature: at or below 0°, metachloral is the sole product, whilst at 40°, a relatively large amount of chloralide is also formed.

Both isomerides show the characteristic properties of true paraldehydes: they have sharp melting points, and are readily soluble in organic solvents, though insoluble in hot or cold water. Cryoscopic molecular-weight determinations in benzene show each to be trimeric, and although they dissociate into chloral on distillation under ordinary pressure, they distil unchanged under a pressure of 15 mm. The less soluble and more soluble forms are termed α- and β-parachloral, respectively.

These two isomerides and metachloral are formed independently, for in the presence of sulphuric acid none is converted into either of the others. It seems probable that the isomerism of α- and β-parachloral is of the *cis-trans* type, corresponding to the two possibilities in the paraldehyde ring, one having all three trichloromethyl residues on the same side of the plane of the ring, and the other having two on one side and one on the other. Isomerism which has similarly been attributed to *cis-trans* forms has been observed in parabromopropaldehyde (Franke, *Annalen*, 1907, **351**, 421), in trichloralimide, $(CCl_3{\cdot}CH{:}NH)_3$ (Béhal and Choay, *Ann. Chim. Phys.*, 1892, **26**, 7, 34), and in the trithioaldehydes, $(R{\cdot}CH{:}S)_3$ (Baumann and Fromm, *Ber.*, 1891, **24**, 1426), and in the last case this type of isomerism has been confirmed, since on oxidation the *cis*-form gives only one disulphone-sulphide, whereas the *trans*-form gives two. One form is converted into the other by the action of acetyl chloride, iodine, etc. Attempts to effect interconversion of the two parachlorals by the same means have been unsuccessful, however.

It is noteworthy that this is the first time that a meta-form and two isomeric para-forms of the same aldehyde have been obtained. The assumption that the relation of the meta- and para-forms is that of *cis-trans* isomerides (compare *Ber.*, 1907, **40**, 4341) can thus no longer be accepted, at least in the case of chloral.

Paradichloroacetaldehyde does not appear to exist in isomeric forms, for sulphuric acid converts it into a single compound, which decomposes when kept for more than a few hours in contact with the acid; it is possible, however, that the failure to isolate a second isomeride is due to its still more rapid decomposition.

Butylchloral, $CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CHO$, like chloral, forms two isomeric polymerides of the para-type when kept in contact with excess of sulphuric acid; these differ in solubility and can be separated by fractional crystallisation from acetic acid. The terms α- and β- may be applied to the less soluble and more soluble

forms as before. In properties they closely resemble the parachlorals, being colourless, crystalline, sharp-melting compounds, soluble in organic solvents, but insoluble in water. They are trimeric, and can be distilled unchanged under a pressure of 15 mm., but dissociate into butylchloral on distillation under ordinary pressure.

It may be noted that the α-forms of parachloral, parabutylchloral, and trichloralimide all crystallise in the orthorhombic system. Béhal and Choay (*loc. cit.*) infer from the crystal symmetry a corresponding molecular symmetry, and designate the α-form "*cis*" and the β-form "*trans*"; but this conclusion seems hardly justifiable.

Butylchloral appears not to form a polymeride of the meta-type; in fact, no meta-polymerides of chloro- or bromo-aldehydes have been observed outside the acetaldehyde group.

EXPERIMENTAL.

Preparation of α- and β-Parachloral.—The most suitable conditions for the preparation of these isomerides are (*a*) a temperature of 15—20°, and (*b*) a large excess of sulphuric acid, and it appears to be essential that the chloral should first dissolve, for metachloral is formed as a crust when a layer of chloral is left floating on the surface of the acid.

Powdered chloral hydrate (100 g.) was added slowly to concentrated sulphuric acid (1000 g.), each portion being shaken until dissolved. On standing for a few hours at the ordinary temperature, a mixture of the three polymerides with chloralide began to separate as a white powder. After 3 days, this solid was filtered off, washed with hot water until the smell of chloral could no longer be recognised, dried, powdered, and extracted with boiling alcohol (100 c.c. to 50 g. of product). The chloralide, which separated from the cold extract, was removed, and cold water added to the filtrate. The colourless precipitate was separated, dried, and boiled for a few seconds with sufficient alcohol to dissolve half of it; evaporation of the extract gave a residue rich in the β-form, and the two solids were then repeatedly recrystallised from alcohol until the two forms were obtained pure and of constant m. p.

α-Parachloral crystallises from boiling alcohol in compact, colourless, rhombic crystals (Found: Cl, 72·02; *M*, cryoscopic in benzene, 423. $C_6H_3O_3Cl_9$ requires Cl, 72·16%; *M*, 442). It melts at 116° *

* It may be noted that this m. p. is very near to that of chloralide (115—116°), which, however, boils at 272° without change. The mixed m. p. of the two may be as low as 85—90°. The monoclinic crystalline form of chloralide (*Z. Kryst.*, 1877, **1**, 594) is quite different from the rhombic form of α-parachloral. Further, chloralide is decomposed by boiling aqueous alkalis.

and boils at 223°/760 mm. The b. p. was determined by the capillary-tube method; in an ordinary distillation apparatus the b. p. rises, owing to decomposition, whilst a thermometer in the vapour registers 98·0°, the b. p. of chloral. Even in a vacuum distillation apparatus under 15 mm. pressure the boiling point was found not to be constant, as some decomposition occurred, but a quantity of unchanged α-parachloral collected in the condenser.

Dr. T. V. Barker, of Brasenose College, has very kindly examined the crystals, and reports that they are orthorhombic, as shown in Fig. 1. The forms developed were *c* (001), *o* (111), and *m* (110). The axial elements, $a : b : c = 0{\cdot}8801 : 1 : 1{\cdot}4505$, were computed from the following mean measurements derived from two crystals:

$$mm \quad (110 : 1\bar{1}0) = 84° \, 42', \quad co \quad (001 : 111) = 65° \, 31'.$$

β-*Parachloral* crystallises from alcohol in long, colourless prisms (Found: Cl, 71·95%; *M*, cryoscopic in benzene, 420), too slender to

FIG. 1.

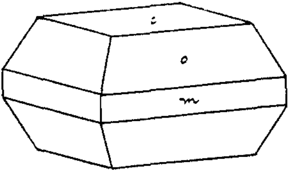
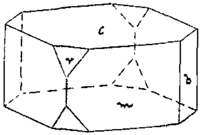


FIG. 2.



admit of measurement. It melts at 152° and boils at 250° (in the capillary tube). Its behaviour on distillation is similar to that of the α-form.

The yield of α- and β-parachloral obtained as above is not more than 1% of the chloral taken: about 2% of chloralide is also formed. These polymerides have none of the characteristic properties of chloral: they are odourless, stable to boiling aqueous alkalis, and do not react with phenylhydrazine or potassium cyanide.

Preparation of α- and β-Parabutylchloral.—In order to obtain a good yield of these polymerides, not less than 6 parts by weight of concentrated sulphuric acid to one part of butylchloral hydrate should be used. With a smaller amount polymerisation is slow, and this probably explains why Willcox and Brunel (*J. Amer. Chem. Soc.*, 1916, **38**, 2538), who used sulphuric acid for dehydrating butylchloral hydrate, failed to observe the formation of the polymerides. 150 g. of concentrated sulphuric acid were poured on 25 g. of

powdered butylchloral hydrate and shaken until a homogeneous brown liquid was formed. In about 2 hours the solid polymerides began to separate, and after standing with occasional shaking for about two days, the mixture became almost solid. Ice was then added, and the caked product which separated was broken up, thoroughly washed with hot water until the smell of butylchloral could no longer be detected, dried, and fractionally crystallised from acetic acid. The total yield of the two isomerides before separation was about 80% of the butylchloral taken.

α-Parabutylchloral crystallises from boiling acetic acid (in which it is moderately soluble) or from boiling alcohol (in which it is sparingly soluble) in compact, colourless, rhombic crystals, m. p. 180°, b. p. 255°/760 mm. (in the capillary tube) (Found: Cl, 60·6; *M*, cryoscopic in benzene, 484. $C_{12}H_{15}O_3Cl_9$ requires Cl, 60·66%; *M*, 526). Its behaviour on distillation under atmospheric pressure or in a vacuum resembles that of α-parachloral.

Mr. W. R. C. Curjel, of Keble College, has kindly examined the crystals, and reports that they are orthorhombic (Fig. 2). The axial elements are $a : b : c = 0{\cdot}8209 : 1 : 1{\cdot}4460$. The forms observed were *c* (001), *b* (010), *m* (110), *r* (101), and, less frequently, *o* (111). Mean values for the interfacial angles are:

$110 : 1\bar{1}0 = 78° \ 46'$	$110 : 111 = 23° \ 35'$
$110 : 101 = 47° \ 46'$	$101 : 111 = 35° \ 24'$
$001 : 101 = 60° \ 22'$	

β-Parabutylchloral crystallises from boiling acetic acid or alcohol (in which it is considerably more soluble than the α-form) in clusters of very small, colourless crystals (Found: Cl, 60·6%; *M*, 479), m. p. 157°, b. p. 233°/760 mm. (capillary tube). In properties and behaviour on distillation it closely resembles the polymerides already described.

Preparation of Anhydrous Butylchloral.—In order to attempt the preparation of a meta-polymeride, it was necessary to prepare anhydrous butylchloral from the hydrate. Neither the method of Willcox and Brunel (*loc. cit.*), who used sulphuric acid as dehydrating agent, nor that of Pinner (*Ber.*, 1870, **3**, 383), who distilled the hydrate in a stream of dry hydrogen chloride, was found satisfactory.

A suitable method is to distil the hydrate with about half its weight of acetic anhydride under a short fractionating column. A considerable portion of acetic acid distils at 120—130°, and the thermometer then rises rapidly to 165° (the b. p. of butylchloral), at which it remains constant practically till the end of the distillation. The fraction which distils at 165° is redistilled and dried in a vacuum desiccator. The distilling apparatus should be thoroughly dry,

and the receiver protected by a calcium chloride tube, to prevent re-formation of the hydrate.

The anhydrous aldehyde is also conveniently prepared by distilling the dry polymerides under ordinary pressure; they need not be separated for this purpose, and are converted quantitatively into the unimolecular form.

Action of hydrogen chloride. Since mono- and di-chloroacetaldehyde are readily converted into meta-polymerides nnder the influence of hydrogen chloride (which also induces the formation of metachloral from chloral, though in this case it is mnch less effective than sulphuric acid), the prolonged action of hydrogen chloride in the cold on butylchloral was investigated. The chloral was saturated with the dry gas and sealed up, but no action occurred even on standing for a long period. A similar experiment was then carried out with butylchloral alcoholate (which absorbs more of the acid), the mixture being well cooled in order to avoid formation of the acetal (compare Freundler, *Bull. Soc. chim.*, 1907, **1**, 201), but no action occurred.

Action of pyridine. Chloral is rapidly converted into metachloral in the presence of $\frac{1}{12}$ mol. of pyridine (Böeseken, *Rec. trav. chim.*, 1913, **32**, 112); 9 g. of butylchloral were therefore sealed up with 0·4 g. of pyridine, the two liquids being readily miscible. After standing for 5 days, the liquid had turned dark brown, and 1·5 g. of a white solid had separated. This was filtered off and washed with a little cold alcohol and hydrochloric acid; it proved to be a mixture of the two parabutylchlorals.

THE QUEEN'S COLLEGE LABORATORY,
OXFORD. [*Received, July* 31*st*, 1928.]

CCCLX.—*The Formation of Liesegang Rings as a Periodic Coagulation Phenomenon.*

By ERNEST SYDNEY HEDGES and ROSALIND VENETIA HENLEY.

DURING the past 32 years, a vast amount of experimental work has been performed on the production of stratified precipitates in gels, and from this work there emerges the important fact that the phenomenon is of a general nature; indeed, it is probable that, given the right conditions, rhythmic banding of a precipitate can be formed from any pair of interacting salts. Most of the numerous theories which have been advanced to account for the observed phenomena apply only to the particular case studied (see Hedges and Myers, "The Problem of Physicochemical Periodicity," 1926,

E. Arnold and Co.), but reference may be made to the four most important theories which are of general applicability, *viz.*, those of Wilhelm Ostwald ("Lehrbuch der allgemeinen Chemie," Leipzig, 2nd edn., 1891, ii, 778), Bradford (*Biochem. J.*, 1916, **10**, 169; 1917, **11**, 14), Dhar and Chatterji (*Kolloid-Z.*, 1922, **31**, 15; 1925, **37**, 2), and Wo. Ostwald (*ibid.*, 1925, **36**, 380).

The reactions which give rise to these banded precipitates are often designated as "rhythmic" or "periodic," but there is nothing to suggest that the reaction–time curve is periodic, and it is therefore proposed to apply the term "periodic structures" to the cases under discussion, and to restrict the term "periodic reactions" to chemical processes where it can be shown that the reaction velocity varies periodically. One of the aims of the present research has been to obtain evidence on this aspect of the matter by determining whether the bands of precipitate are formed primarily in the diffusing wave-front, or whether the banding is a secondary phenomenon occurring after formation of the substance. We believe that we have definitely established the truth of the latter view.

EXPERIMENTAL.

The System Silver Dichromate–Gelatin.

When a large drop of 20% silver nitrate solution is placed on a 10% gelatin gel containing 0·4% of potassium dichromate, it is generally observed that in the initial stages of diffusion concentric rings of precipitate are formed at the edge of the diffusing wave-front, and somewhat later the rings are surrounded by a pale yellow fringe. The fringe increases gradually in breadth, often to the extent of 1 cm. or more.

By conducting the experiment in a test-tube, down the outside of which a thin strip of paper is pasted, and marking the positions of the extreme edge of the yellow fringe and of the last red ring after various time intervals, it can readily be shown that the rings are formed some distance behind the diffusing wave-front. These observations cannot be taken as evidence that the production of rings is a secondary effect, since the nature of the pale yellow fringe is not definitely known. Friend (J., 1922, **121**, 472) regards it as colloidal silver chromate, whereas according to Riegel and Reinhard (*J. Physical Chem.*, 1927, **31**, 713) it consists of silver chloride, formed by the sodium chloride present as an impurity in commercial gelatin. It is stated that no such haze is produced if the gelatin has previously been washed thoroughly. Our observations support the view of Riegel and Reinhard, but we cannot agree with them that the production of red rings of silver dichromate

is dependent on the substructure due to the chloride; for we find that after the chloride in a gelatin sol has been completely precipitated by dilute silver nitrate solution and the stirred liquid allowed to set to a structureless gel with addition of potassium dichromate, good rings are produced by allowing 20% silver nitrate solution to diffuse into the gel. Further, if a drop of 20% silver nitrate solution be placed on the yellow fringe in the ordinary diffusion experiment, an independent ring system develops immediately, which can bear no relation to the pre-existent substructure.

Experiments to be described later have shown that when very dilute solutions of silver nitrate and potassium dichromate are mixed together in gelatin no precipitate is formed, the product apparently remaining in a colloidal state, protected by the gelatin. A considerable excess of silver nitrate causes coagulation of the colloid to a red precipitate. It seems unlikely, therefore, that silver dichromate is precipitated in the direct chemical reaction during the course of the formation of Liesegang rings, but rather that the first product of the reaction is colloidal silver dichromate, which is afterwards coagulated in rings by excess of the diffusing silver nitrate.

An experiment was devised to separate the chemical reaction and the coagulation into two stages and to determine which stage is responsible for the periodicity. The method consisted in adding to the gelatin–potassium dichromate mixture an equivalent quantity of silver nitrate and, after the mixture had set to a gel, causing 20% silver nitrate solution to diffuse into it. To conduct this experiment, it does not suffice to add directly to the gelatin equivalent quantities of the two reactants, for the chlorides, etc., in the gelatin dispose of some of the silver nitrate preferentially, leaving some potassium dichromate free. It was necessary, therefore, to determine the substances in the gelatin which could react preferentially with silver nitrate. This was done by igniting a weighed amount of gelatin and titrating the aqueous extract of the ash with silver nitrate in presence of potassium dichromate as an indicator. Since the composition of one gelatin leaf differs from that of another from the same source, a large amount of 10% gelatin sol was prepared and 25 c.c. were withdrawn for the analysis, which was thus performed on the same sol as that used for the experiments. The sol (25 c.c.) was evaporated to dryness in a platinum dish and finally heated over the blowpipe until the ash attained a constant weight, which was 1·64% of the weight of dry gelatin. This amount of ash (0·0410 g. in 25 c.c.) was equivalent to 2·95 c.c. of 0·5% silver nitrate solution.

From these data, a sol of silver dichromate in 5% gelatin was

FIG. 1.

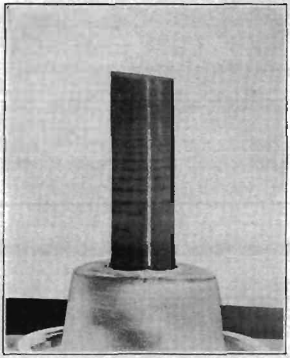
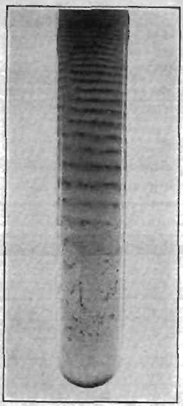
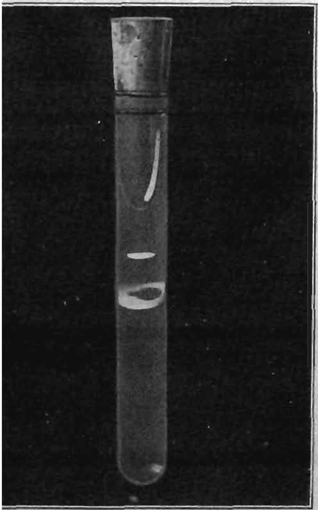
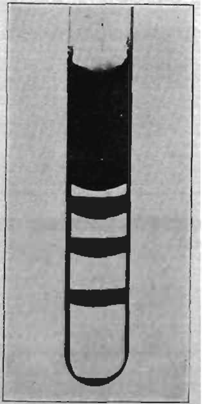


FIG. 2.







made by mixing (*a*) 20 c.c. of 10% gelatin + 20 c.c. of 0·2871% potassium dichromate solution with (*b*) 20 c.c. of 10% gelatin + 14·74 c.c. of 0·5% silver nitrate solution. After the mixture had set to a gel in a number of test-tubes, 20% silver nitrate solution was poured over the top: the resulting periodic structure due to coagulation is reproduced in Fig. 1. The bands are as well defined as those produced by chemical reaction, and, moreover, they are subject to the same peculiarities; for example, the bands in one tube formed a spiral. The silver dichromate was not coagulated by diffusing a saturated solution of potassium dichromate into the gel.

In a second series, a 30% excess of silver nitrate was added to silver dichromate in gelatin. Bands were produced by diffusing 20% silver nitrate solution into the mixture, but they were not so well marked as in the former case, a considerable amount of precipitation occurring in the spaces between the bands. In this system, bands were formed by the interdiffusion of a saturated solution of potassium dichromate, affording confirmation that there was excess of silver nitrate in the gel.

The experiments indicate that the banding is not concerned with the chemical reaction, but is a secondary phenomenon occurring after the reaction. The two stages have been separated, the chemical reaction having been carried out first without periodic phenomena, and a stratified precipitate being produced in the second stage of coagulation by excess of silver nitrate.

Measurement of the Critical Concentration of Silver Nitrate.

The experiments described in this section were designed, not only to gain an idea of the critical concentration of silver nitrate necessary to coagulate silver dichromate under the conditions prevailing in the former experiments, but also to test the suggestion made by Hedges and Myers (*op. cit.*, p. 27), that the formation of periodic structures may have its explanation in the periodic opacity phenomenon of Holker (*Proc. Roy. Soc.*, 1923, *A*, **102**, 710). According to this author, the opacity of a precipitated colloid is in many cases a periodic function of the concentration of the precipitating electrolyte, and the suggestion was made (Hedges and Myers, *op. cit.*) that, since in the formation of a periodic structure the advancing diffusion wave is subject to a progressive dilution, a series of opacity bands is to be expected, corresponding with the peaks of Holker's curves. If such be the case, *one would expect that, when a series* of test-tubes containing colloidal silver dichromate in gelatin is treated with progressively increasing concentrations of silver nitrate (each tube receiving a higher concentration than its predecessor), then precipitation would occur in some tubes and not in others,

the arrangement being periodic throughout the series, but the experiments do not lend any support to this view.

To each of a series of tubes containing 5 c.c. of silver nitrate solution were added 5 c.c. of a sol prepared by mixing equal volumes of 0·125% silver nitrate in 5% gelatin and 0·1435% potassium dichromate in 5% gelatin. Silver nitrate solutions were examined over the concentration range 0·1% to 3·0%. All the solutions up to and including 0·29% silver nitrate remained a clear yellow after addition of the silver dichromate–gelatin mixture, but a red precipitate was produced in the 0·30% solution. A further series was conducted with twelve tubes in which the concentration was varied from 0·288% to 0·299% at intervals of 0·001%. At first sight it seemed that there was actually a periodic change, produced by progressively increasing concentration. It appears, however, that the production of precipitate in any one tube is fortuitous, depending, for instance, on the nuclei provided by the tube and on the rate of mixing. The whole series was repeated three times in tubes which had previously been soaked thoroughly in a mixture of nitric and chromic acids. In these experiments there was a complete lack of correspondence in the behaviour of individual tubes: those concentrations which were the first to give a red precipitate in one experiment were the last to retain their yellow colour in the next. No reliance can be placed, therefore, on values of critical concentration measured in terms of less than 0·01%. The critical concentration required to coagulate colloidal silver dichromate under the conditions described may be taken as 0·29%.

We believe that these observations offer a satisfactory explanation of the unpublished experiment performed by Holker and reported by Hedges and Myers (*op. cit.*, p. 27).

The System Lead Iodide–Agar.

Periodic structures can readily be obtained by diffusing 30% lead nitrate solution into an agar gel containing potassium iodide (see Hatschek, "Laboratory Manual of Colloid Chemistry," 1925, p. 144). This system has been treated in the same manner as the preceding one, and it has again been shown that the chemical reaction can be carried out first, the bands being obtained subsequently by coagulation.

Equal volumes of 1% agar solutions containing 0·6% of potassium iodide and 0·6% of lead nitrate (equivalent weights) were mixed while hot and allowed to set in test-tubes. On cooling, the lead iodide did not separate, although its solubility in water was exceeded many times. However, when kept for some days, such gels gave a yellow deposit in patches on the side of the test-tube.

30% Lead nitrate solution was poured into the space above the gel in two tubes; after 2 days, five successive discs had appeared in the tube. These discs did not reach to the walls of the tube, but were suspended in the gel; the first two were sharply defined, and the remainder more diffuse; the mean distance between the bands was about 1 cm., becoming greater with increasing depth in the tube.

Diffusion of 20% potassium iodide solution into another tube gave a ring system comparable in every respect with that produced by chemical reaction. Within an hour, numerous fine bands were visible. It seems that in this instance either of the reactants serves as a coagulating agent, but potassium iodide is much more effective than lead nitrate.

In order to eliminate any possible complications due to the concomitant production of potassium nitrate in making up the gel mixture, the experiments were repeated and extended in agar gels containing lead iodide in absence of other electrolytes. These were prepared by dissolving recrystallised lead iodide in 1% agar solution at 100°, and allowing it to cool. A few trials indicated that the cooled gel would hold as much as 0·2% of lead iodide, although the solubility in water at the ordinary temperature is only 0·04%.

A number of test-tubes containing 1% agar gel with 0·2% lead iodide were treated with various diffusing agents. Periodic structures, exactly similar to those described for gels prepared by the former method, were produced when 30% lead nitrate or 20% potassium iodide was the diffusing solution. An example of the bands produced when potassium iodide diffused into the gel is given in Fig. 2.

Other solutions were allowed to diffuse into the above mixture and bands were observed in some cases; 20% silver nitrate, 20% sodium carbonate, and a saturated solution of mercuric chloride gave rings, but 30% aluminium sulphate, 20% cupric chloride, dilute nitric acid, and ammonia (*d* 0·880) gave none.

The System Magnesium Hydroxide–Gelatin.

The periodic structure produced when ammonia diffuses into a gelatin gel containing magnesium chloride has been described by Popp (*Kolloid-Z.*, 1925, **36**, 208), and the system is unique in that it produces only a small number of sharply defined, relatively massive bands.

For coagulation experiments, a 6·5% gelatin gel was used, containing 5% of crystallised magnesium chloride with an equivalent amount of ammonia. The magnesium hydroxide remained in colloidal solution under these conditions. The mixture was allowed to set to a gel in test-tubes, and ammonia solution (*d* 0·880) was

poured over each. After 4 days, the periodic structure portrayed in Fig. 3 was produced. These rings are comparable with those produced by direct diffusion of strong ammonia into gelatin containing magnesium chloride alone. The photograph was taken by transmitted light, and the white rings of magnesium hydroxide therefore appear dark and the clear spaces white.

Chemical Analysis of the Periodic Structure.—The system magnesium hydroxide–gelatin lends itself admirably to investigation by means of chemical analysis, as a result of the macroscopic nature of the effect. Some analyses (for which no great accuracy is claimed) were therefore undertaken with this system, the object of the examination being solely to determine whether a very uneven distribution of material between the bands and spaces occurs, or whether these approximate to each other in composition. It has often been supposed that the actual amount of product in equal volumes of the bands and the clear spaces is in many cases nearly equal (compare Hatschek, *British Association*, *Second Colloid Report*, 1918), but the results of the present analysis show that the composition of the bands differs widely from that of the clear space.

According to Ostwald (*Kolloid-Z.*, 1925, **36**, 380), Popp carried out some analyses of the system under discussion, and found the concentration of chlorine ions in the bands directly after formation to be almost double that in the original gel, but experimental details were not given. We reproduce our results, since they not only differ quantitatively from those of Popp, but are in the opposite sense. The divergence is probably to be explained by the fact that, whereas the determinations reported by Ostwald were made on new-born rings, those now given refer to the completed structure a week or more old. The structures were prepared by diffusing ammonia (*d* 0·880) into 7·5% gelatin gel containing 5% of crystallised magnesium chloride. Such a concentration of gel was necessary to secure rigidity in cutting and handling, although Popp recommends a 3% gel for giving the best bands.

The following device for removing the gels from the tubes was found eminently satisfactory. After excess of the diffusing liquid had been poured away, a groove was cut by means of a glass knife so as to encircle completely the tube near the lower, closed end. The end of the tube could be removed as a cap by applying a red-hot splinter of glass to the groove. The tube was then dipped for 1 second into water at about 80°, which had the effect of loosening the gelatin adhering to the glass, and the entire structure could readily be blown out of the tube. All other methods of extricating the gels failed because of the strong adherence of gelatin to glass. Agar gels can conveniently be removed by cracking open the tubes.

The structures were cut up into bands and clear spaces by means of a safety-razor blade.

The white bands were found to be fairly hard and relatively heavy (the density was about 1·7 times that of the clear space), and were readily detached in the form of pastilles from the intervening gel spaces. *Three bands and the two enclosed clear spaces* were chosen for the analysis. In order to gain an indication of the distribution of material in equal volumes of band and space as well as in equal weights, the length of gel taken was measured in addition to the weight. The error of measurement of the length was great, however, and much more trust may be placed upon the results expressed per unit weight of gel.

Determination of magnesium. The method was to heat the gel gently in a platinum crucible until water had ceased to be driven off, and later over the blowpipe until a constant weight of magnesium oxide was obtained. In the meantime, the ammonium chloride volatilised. The weight of gelatin ash was subtracted from the total weight. Slight alterations due to differences in swelling, etc., may be disregarded. The results are summarised in the following table :

Determination of MgO (structure 7 days old).

	Length of gel (mm.).	Wt. of gel (g.).	Wt. of MgO.	G. of MgO per mm.	G. of MgO per g. of gel.	Relative amounts of MgO, per unit vol.	per unit wt.
Band	5	1·47	0·046	0·009	0·031	20	12
Clear space	20	3·51	0·009	0·00045	0·0026	1	1

Determination of chloride. The gel was made up to 100 c.c. by addition of dilute nitric acid. Direct titration with silver nitrate and potassium thiocyanate yielded poor results, as the end-point was changed by the presence of the gelatin. A method similar to that used for the determination of chlorides in blood was therefore adopted. The gelatin was precipitated by means of tungstic acid, and after filtration, silver nitrate and nitric acid were added in excess, and portions of the solution were titrated with standardised potassium thiocyanate. A good end-point was obtained with the solution from the clear space, but that from the bands gave a poor end-point. The following table contains the results :

Determination of chloride (structure 9 days old).

	Length of gel (mm.).	Wt. of gel (g.).	Total chloride.	G. of chloride per mm.	G. of chloride per g. gel.	Relative amounts of chloride per unit vol.	per unit wt.
Band	7	1·543	0·0060	0·00086	0·0039	1·0	1·0
Clear space	26	4·240	0·054	0·00207	0·0127	2·4	3·26

The analyses show that the amount of precipitate contained in the bands is 12 times as great as that present in an equal weight of clear space, whereas the chloride content of the bands is less than one-third of that of the clear space. The equivalent ratio, $\frac{1}{2}$Mg : Cl, is 14·0 : 1 in the bands, and 1 : 2·8 in the clear space.

It may be observed that the total chloride in the gel is not equivalent to the total magnesium. The missing chloride was found in the diffusing solution standing above the gel, indicating that the soluble product, ammonium chloride, diffuses out of the gel and into the ammonia solution. Experiments were therefore conducted in which this outward diffusion was prevented by dissolving in the diffusing ammonia solution sufficient ammonium chloride to give a concentration just equal to that produced in the gel by reaction. Excellent bands developed in these tubes, so that the outward diffusion of ammonium chloride is not essential to the production of the periodic structure.

Other experiments were carried out, in which equivalent solutions of magnesium chloride and ammonia were mixed in 7·5% gelatin, and water was placed over the gel, in order to see whether, with the outward diffusion of the ammonium chloride, the magnesium hydroxide would be precipitated in bands; but no precipitate was formed.

The "diffusion-wave" theory of Wo. Ostwald (*loc. cit.*) is founded largely on observations on the magnesium hydroxide system. The theory is admitted to be applicable only to rhythmic structures produced by chemical reaction, and the existence of three diffusion waves (those of the two reacting substances and of the soluble product) is postulated. Since the work described in the present paper has shown that essentially similar structures can be produced after the chemical reaction is completed, it would seem that the theory is not very comprehensive. An instance where the diffusion-wave theory appears to fail completely is in the production of rhythmic structures by potassium iodide or lead nitrate diffusing into lead iodide in agar. Here, the greatest possible number of diffusion waves which can be set up is two, and yet the resulting structure does not differ from that produced as the result of chemical interaction of lead nitrate and potassium iodide.

The Periodic Coagulation of Sols of Arsenious Sulphide and Ferric Hydroxide.

As a corollary to the experiments on the production of periodic structures after the chemical reaction has been carried out, it should be possible to obtain such structures by simple diffusion of

a coagulating electrolyte into a sol contained in a gelatin or agar gel. Experiments have been conducted on these lines with sols of arsenious sulphide and of ferric hydroxide in agar gels.

An arsenious sulphide sol was prepared by passing hydrogen sulphide into a solution containing 0·5 g. of sodium arsenite in 500 c.c. of water, and removing the excess of hydrogen sulphide by means of a stream of hydrogen. Three gels containing different amounts of arsenious sulphide were prepared. Gel 1 was made by mixing the arsenious sulphide sol with an equal volume of 2% agar sol; Gel 2 was prepared by diluting the arsenious sulphide to one-half of the original concentration with water, and mixing equal volumes of the diluted sol and 2% agar; and in Gel 3 the arsenious sulphide sol was first diluted to one-fourth of its concentration and then mixed with an equal volume of 2% agar. The diffusing electrolyte was ferric chloride or aluminium sulphate at concentrations of 30, 10, 5, and 1%.

In these systems the process of diffusion was slow, and results of observations made after 20 days are given below. With ferric chloride as the diffusing agent, no bands were produced in Gel 3 for any of the concentrations, Gel 2 produced poor bands, and Gel 1 good bands. The best results were obtained with 5 and 1% of ferric chloride. The formation of the bands, therefore, is favoured by a high concentration of colloid and a low concentration of electrolyte. As shown below, a still higher concentration of arsenious sulphide sol is unfavourable to band formation, suggesting that there is an optimum concentration.

In transmitted light the periodic structure appeared as a number of dark bands across the test-tube, which were just discernible in reflected light by their deeper yellow colour. The spaces between the bands contained a considerable amount of arsenious sulphide.

The most characteristic feature of these structures is the fact that the distance between successive bands *decreases*, whereas in most periodic structures the successive bands become more widely spaced throughout the diffusion. This fact agrees with the observation that the mean distance between the bands is greater the more concentrated the diffusing solution, and is contrary to the usual observation. With 30% and 1% ferric chloride, the mean distances between the bands were respectively 9 mm. and 3 mm. One such instance of a periodic structure has been recorded (Davies, *J. Amer. Chem. Soc.*, 1917, **39**, 1312), which occurs in the precipitation of mercury when mercurous nitrate diffuses into sodium formate contained in gelatin.

The results were similar in the experiments with aluminium sulphate as the coagulating agent. Bands were observed only in

Gel 1, and the best results were obtained in the tubes containing the lower concentrations of diffusing agent. The distance between successive bands decreased, and the spacing was wider the more concentrated the solution; 10% aluminium sulphate produced 7 bands occupying 33 mm. along the tube, and 1% aluminium sulphate produced 6 bands occupying 20 mm.

To ensure that these bands were really caused by coagulation of the arsenious sulphide sol, control experiments were conducted in which the solutions were allowed to diffuse into (*a*) 1% agar gel alone, (*b*) 1% agar containing sodium sulphide equal in amount to that produced together with arsenious sulphide in the sols discussed above. No bands were produced in any of these tubes.

A further precaution was taken, in that the experiments were repeated with colloidal arsenious sulphide prepared in almost complete absence of electrolytes. 0·5 G. of arsenious oxide was added to boiling water with two drops of 2*N*-sodium hydroxide to aid the dispersion. Dissolution occurred readily and hydrogen sulphide was passed through, the excess being removed by means of hydrogen. Two concentrations of sol were prepared; in the first, equal volumes of arsenious sulphide sol and 2% agar were mixed, and in the second the arsenious sulphide sol was diluted to one-half of its original concentration with water before being mixed with an equal volume of the agar sol. The diffusing agents were ferric chloride, aluminium sulphate, and magnesium chloride at concentrations of 10, 5, 1, and 0·5%. After 12 days, good bands had formed only in the more dilute sol, especially with ferric chloride at concentrations of 0·5 and 1%. The more concentrated sol gave zonal turbidities rather than definite bands, the best examples occurring with 10% magnesium chloride and 0·5% ferric chloride and aluminium sulphate. The decreasing distance between successive bands was again noticed in these systems.

Some experiments of the same type were carried out on undialysed sols of ferric hydroxide, prepared by the ammonium carbonate method (Hatschek, "Laboratory Manual of Colloid Chemistry," 1925, p. 46). Three concentrations of sol were used, the original concentration being diluted 10, 20, and 40 times respectively. The gels were prepared by mixing equal volumes of the sols with 2% agar and allowing them to set. The coagulating electrolytes used were 30% and 10% sodium sulphate, 20% and 5% sodium arsenite, and 20% and 5% ammonium carbonate. After 13 days, periodic structures had appeared only in the tubes containing the sol of middle concentration, banded turbidities being produced when the coagulating electrolyte was 20% or 5% sodium arsenite or 5% ammonium carbonate. In the tube containing 5% sodium arsenite,

the distances between successive bands were 15, 12, 10, 9, and 7 mm., a decrease again being apparent. With 20% sodium arsenite the bands made their first appearance about half-way down the tube, showing that in this case also a dilute coagulating agent is favourable.

Anomalous Structures.

Many investigators of the Liesegang phenomenon have commented on the mal-formations sometimes produced. In many cases these are due to lack of homogeneity of the gel or of some other component of the system. It was found in the present work, for example, that deformed rings of magnesium hydroxide were produced when a crystal of ammonium chloride was dropped into the gel containing magnesium chloride. Some experiments in which 30% lead nitrate diffused into 2% potassium iodide contained in an agar gel produced rings in twins. In another experiment, equal volumes of 2% agar and 5% magnesium chloride were mixed in a test-tube and allowed to set; when ammonia (*d* 0·880) diffused in, a spiral structure of magnesium hydroxide was formed. It was observed that spiral precipitation was not caused directly by helicoid diffusion, but that layers of precipitate reaching half-way across the test-tube were formed alternately on opposite sides, and at different levels; later, these joined to form a spiral. When the bands became more than about 1 cm. apart, they no longer joined up. This effect may be caused by temperature difference due to the exposure of one side of the tube to a draught.

An extreme case of this anomaly was observed in the reverse experiment, in which 50% magnesium chloride solution diffused into a mixture of equal volumes of 2% agar and ammonia containing 5·4 c.c. (*d* 0·880) in 100 c.c.; the first band consisted of a thin disc suspended in the agar, a short way below the surface, which did not reach to the sides of the tube; it was closely followed by an annulus, the space in the middle corresponding with the disc above, as though the disc had thrown its shadow on to the second band. The ring was succeeded by another disc which in its turn was followed by a corresponding ring. The discs and rings were too close together to be photographed, but a similar experiment in which gelatin was used instead of agar is shown in Fig. 4. The disc consisted of a thick, firm pastille, and was separated some distance from its corresponding ring. The gelatin melted during a warm week-end, before any further discs and rings had formed. This type of structure may be caused by the unequal rate of setting of the gel in the middle and near the walls of the

Summary.

The production of periodic structures of silver dichromate and of magnesium hydroxide in gelatin, and also of lead iodide in agar, has been studied. In each case, by mixing equivalent quantities of the reactants in the gel, and then superimposing a strong solution of the diffusing electrolyte, it has been possible to separate the chemical reaction from the formation of precipitate. Since the rings produced in these experiments are comparable with those produced by chemical reaction, it follows that the formation of periodic structures is a coagulation phenomenon taking place after the chemical reaction. Periodic structures are to be distinguished, therefore, from periodic reactions.

The critical concentration of silver nitrate required to coagulate colloidal silver dichromate has been measured, and the results are discussed in connexion with Holker's periodic precipitation experiments.

A chemical analysis of a periodic structure of magnesium hydroxide in gelatin has been conducted, and the results show that the ratio of magnesium hydroxide contained in the bands to that in the clear spaces is about 12 : 1; the corresponding ratio for ammonium chloride is about 1 : 3.

Periodic coagulation of sols of arsenious sulphide has been effected by diffusing solutions of ferric chloride and aluminium sulphate into the sol contained in 1% agar gel, and similar results have been obtained in the coagulation of colloidal ferric hydroxide by sodium arsenite and by ammonium carbonate. In these cases, there is an optimum concentration of colloid, and band formation is favoured by a dilute diffusing electrolyte.

We are indebted to Professor J. F. Spencer for affording research facilities to one of us (R. V. H.).

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CCCLXI.—*Co-ordination Compounds of Quinquevalent Molybdenum: Complex Thiocyanates.*

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ONE of the most sensitive methods for the detection and estimation of small amounts of molybdenum is the so-called potassium thiocyanate reaction, based on the observation of Braun (*Z. anal. Chem.*, 1863, **2**, 36; 1867, **6**, 86) that a mineral acid solution of molybdenum

trioxide containing an alkali thiocyanate turns a deep red on the addition of a reducing agent such as zinc or stannous chloride. Even at the present time the constitution of the substance responsible for the red coloration is not known with certainty. It can, however, be almost quantitatively extracted from its aqueous solution by ether. Addition of pyridine or quinoline to the ethereal extract gives dark red oils which, on standing, or boiling with alcohol, yield brownish-red crystalline substances to which the formula $R_2Mo(OH)_2(CNS)_3$, where $R = C_5H_5N$ or C_9H_7N, was assigned (Rosenheim and Koss, *Z. anorg. Chem.*, 1906, **49**, 148; Sand and Burger, *Ber.*, 1906, **39**, 1761).

A more rational formulation on the basis of Werner's theory would be $R_2[MoO_2(CNS)_3]$, where $R = C_5H_6N$ or C_9H_8N, which suggests that possibly the red colour in the ethereal solution is due to the complex acid $H_2[MoO_2(CNS)_3]$. The isolation of this acid was attempted by Rosenheim and Koss (*loc. cit.*), who produced a deep red solution by boiling molybdenum trioxide with thiocyanic acid (10%) under reflux, and obtained from the filtrate by evaporation an almost black, hygroscopic residue of variable composition, but probably chiefly containing $Mo(OH)_2(CNS)_3$ (Abegg, "Handbuch," IV, 1, p. 541). By dissolving the pyridinium salt

$$(C_5H_6N)_2[MoO_2(CNS)_3]$$

in thiocyanic acid, Rosenheim and Koss obtained insoluble, dark green, rhombic crystals to which they gave the composition $Mo(OH)_2(CNS)_5H_2(C_5H_5N)_2$, which is better written as

$$(C_5H_6N)_2[MoO(CNS)_5],H_2O.$$

As the above summary indicates, our knowledge concerning thiocyanates of quinquevalent molybdenum is still far from complete, and in view of their interest in both analytical and theoretical chemistry, further investigation seemed desirable.

Salts of the Type $R_2[MoO_2(CNS)_3]$.—In the present investigation, the above method for the preparation of the complex pyridinium and quinolinium salts has been discarded in favour of the reaction between ammonium thiocyanate and salts of the type $R_2[MoOCl_5]$; Sand and Burger (*loc. cit.*) mentioned this method but gave no experimental details. In a previous communication (J., 1927, 2145) the preparation and properties of the green crystalline salts $R_2[MoOCl_5]$ were described, and it was shown from physico-chemical data that such salts undergo extensive decomposition in aqueous solution. Qualitative evidence of this decomposition is seen in the fact that these green salts dissolve in water giving brown acidic solutions from which it is impossible satisfactorily to obtain the original salt by recrystallisation. It is not unexpected, therefore, that in aqueous solution the reaction between ammonium thiocyanate and complex

salts of the type $R_2[MoOCl_5]$ does not give products in accordan with the equation: $5NH_4CNS + R_2[MoOCl_5] = R_2[MoO(CNS)_5]$ $5NH_4Cl$, but yields instead insoluble substances of the ty $R_2[MoO_2(CNS)_3]$. As shown later, salts of the type $R_2[MoO(CNS)$ can only be produced in presence of excess of thiocyanic acid.

The formation of the compounds $R_2[MoO_2(CNS)_3]$ is addition evidence for the scheme of ionisation and hydrolysis mentioned our previous communication:

$$R_2[MoOCl_5] + H_2O \rightleftharpoons R[MoOCl_4,H_2O] + RCl \quad . \quad (1)$$
$$R[MoOCl_4,H_2O] + H_2O \rightleftharpoons [MoOCl_3,2H_2O] + RCl \quad . \quad (2)$$
$$[MoOCl_3,2H_2O] + H_2O \rightleftharpoons [MoO(OH)Cl_2,2H_2O] + HCl \quad (3)$$
$$[MoO(OH)Cl_2,2H_2O] + H_2O \rightleftharpoons [MoO(OH)_2Cl,2H_2O] + HCl$$
$$\rightleftharpoons [MoO_2Cl,3H_2O] + HCl \quad . \quad . \quad (4)$$
$$[MoO_2Cl,3H_2O] + H_2O \rightleftharpoons [MoO_2OH,3H_2O] + HCl \quad . \quad (5)$$

When stage (4) is reached, in all probability the reaction in th presence of ammonium thiocyanate takes the following course:

$$[MoO_2Cl,3H_2O] + NH_4CNS \longrightarrow [MoO_2CNS,3H_2O] + NH_4Cl$$
$$2RCl + 2NH_4CNS \longrightarrow 2RCNS + 2NH_4Cl$$
$$2RCNS + [MoO_2CNS,3H_2O] \longrightarrow R_2[MoO_2(CNS)_3] + 3H_2O$$

In this way complex thiocyanates, where $R = C_9H_8N$, C_5H_6N, Tl (ous), have been prepared.

The reaction between aqueous solutions of $(NH_4)_2[MoOCl_5]$ an ammonium thiocyanate may be expressed as follows:

$$[NH_4]_2[MoOCl_5] + 4H_2O \rightleftharpoons [MoO_2Cl,3H_2O] + 2NH_4Cl + 2HCl$$
$$2HCl + MoO_2Cl + 3NH_4CNS \rightleftharpoons H_2[MoO_2(CNS)_3] + 3NH_4Cl.$$

The *dihydrogen molybdenum dioxytrithiocyanate* has been thus pr pared. It is extremely deliquescent, and exhibits a green lustre. concentrated aqueous solution is purple-red, but on further dilutic becomes red, orange, and finally yellow. The concentrated solutio yield purple precipitates with nitrates of silver and thallium, but th dilute yellow solutions give almost white precipitates consistin chiefly of thallous or silver thiocyanate. These reactions indica that whilst in concentrated aqueous solution a complex acid present, on dilution the complex anion undergoes hydrolysis an further ionisation.

Salts of the Type $R_4[Mo_2O_3(CNS)_8]$.—In view of the productio of salts of the foregoing type, it was interesting to discover th when the green salts $[(CH_3)_3NH]_2MoOCl_5$ and $[(CH_3)_4N]_2MoOC$ reacted with ammonium thiocyanate, the products were not reddis brown compounds like the pyridinium and quinolinium derivativ

·f the type $R_2[MoO_2(CNS)_3]$, but purple crystalline *substances* of the mpirical formula $R_4[Mo_2O_3(CNS)_8]$. These octathiocyanates may ›e conveniently considered as bridge compounds having the con-titution

$$R_4\left[{}^{(CNS)_3}_{O}Mo{<}^{\;\;\;O\;\;\;}_{CNS\;\;CNS}{>}Mo^{(CNS)_3}_{O}\right]$$

The basis for such a configuration will be demonstrated later.

Salts of the Type $R_2[MoO(CNS)_5]$.—Rosenheim and Koss (*loc. cit.*), ·ho first discovered this series, describe the preparation of the ne known derivative as follows : " When $(C_5H_5N)_2Mo(OH)_2(CNS)_3$; dissolved in thiocyanic acid, or pyridinium thiocyanate is added irectly to a solution of molybdic acid in aqueous thiocyanic acid, lack, glittering, rhombic needles are obtained which are decomposed y water and dissolve in alcohol and in chloroform with a deep ›d colour." The composition $(C_5H_5N)_2H_2Mo(OH)_2(CNS)_5$ was scribed to the crystals.

The above method was investigated, and after a suitable way of reparing thiocyanic acid had been established, a *pyridinium* com-ound was obtained of the composition $(C_5H_6N)_2[MoO(CNS)_5]$.

Quinolinium, tetramethyl- and *trimethyl-ammonium* salts of this ·pe were also isolated, entirely analogous in formulation to the reen complex chlorides $R_2[MoOCl_5]$. In their properties, however, ılts of the two series exhibited marked contrasts; whilst the chlorides ›adily dissolved in water with considerable decomposition (the ›obable cause of their high solubility), the corresponding black ıiocyanates were almost insoluble. In carefully dried alcohol the ıiocyanates dissolved very readily, whereas the corresponding ›mplex chlorides were almost insoluble in the cold. The formation ' pentathiocyanates by the method described above takes place ; follows :

$$[MoO_2(CNS)_3]R_2 + 2HCNS = [MoO(CNS)_5]R_2 + H_2O.$$

They can also be prepared by addition of the green chlorides to a ›iling solution of thiocyanic acid, the thiocyanate crystallising ımediately on cooling :

$$R_2[MoOCl_5] + 5HCNS \rightleftharpoons R_2[MoO(CNS)_5] + 5HCl.$$

his is a reversible reaction, for by treating the thiocyanate with ›t concentrated hydrochloric acid, it is possible to obtain the ›ntachloride.

The preparation of the ditrimethylammonium and ditetramethyl-nmonium members of the pentathiocyanate series involves the ›tion of thiocyanic acid on the corresponding octathiocyanates,

and is therefore of special interest. The reaction can be represented as follows :

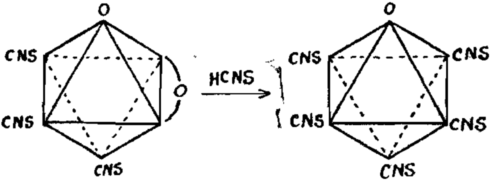
$$R_4\left[\begin{matrix}(CNS)_3\\ O\end{matrix}Mo\begin{matrix}<\!\!\text{——O——}\!\!>\\ CNS \quad CNS\end{matrix}Mo\begin{matrix}(CNS)_3\\ O\end{matrix}\right] + 2HCNS$$

$$\longrightarrow 2R_2\left[\begin{matrix}(CNS)_3\\ O\end{matrix}Mo\begin{matrix}CNS\\ CNS\end{matrix}\right] + H_2O$$

and also seems to indicate that the octathiocyanates possess a symmetrical structure.

The Co-ordination Number of Oxygen.

In a previous communication (J., 1927, 1087) it was mentioned that oxygen, contrary to the view of Werner, did not always occupy only one position in the co-ordination sphere, but that cases did arise in which this bivalent atom must be assigned two positions. A possible illustration of this fact is afforded by the co-ordination compounds of quinquevalent molybdenum. In the complex salts $R_2[MoOCl_5]$ and $R_2[MoO(CNS)_5]$, with oxygen occupying only one position in the co-ordination sphere, the molybdenum has a co-ordination number of six. With related complex substances of the type $R_2[MoO_2(CNS)_3]$ Werner's conclusions would lead to the molybdenum atom being assigned a co-ordination number of five. However, by the action of thiocyanic acid it is a simple matter to transform a salt of the type $R_2[MoO_2(CNS)_3]$ into the type $R_2[MoO(CNS)_5]$, where the molybdenum atom has a co-ordination number of six. It seems questionable whether this reaction involves the change of a five-point into a six-point system, and a more rational formulation would be to assign in both cases a co-ordination number of six to the molybdenum atom. It would then be necessary to consider one oxygen as occupying one position, and the other two positions, in the co-ordination sphere.



Such a configuration clearly demonstrates why one oxygen is reactive, and the other is not. It is also a matter of interest to find that neither in the case of the complex chlorides $R_2[MoOCl_5]$ nor in

that of the corresponding thiocyanates $R_2[MoO(CNS)_5]$ can the oxygen atom be displaced by the highest concentration of acid with the formation of such salts as $R_2[MoCl_7]$ or $R[MoCl_6]$.

It must be noted, however, that salts of the type $R_2[MoO_2(CNS)_3]$ may be represented as $R_4\left[{}^{(CNS)_3}_{\quad O}Mo{<}^{O}_{O}{>}Mo^{(CNS)_3}_{O}\right]$.

In a previous communication the importance of the effective atomic number of the molybdenum atom in determining the stability of its complex salts was emphasised. With the spatial configuration shown in the above diagram it will be seen that in salts of the type $R_2[MoO(CNS)_5]$ and $R_2[MoO_2(CNS)_3]$ the effective atomic number is 49. It is not surprising, therefore, that in aqueous solution these salts exhibit instability, in marked contrast to the great stability of the series $R_4Mo(CN)_8$, where the effective atomic number of the central atom is 54—that of the next inert gas.

EXPERIMENTAL.

Compounds of the Type $R_2[MoO_2(CNS)_3]$.

The green salts of the type $R_2[MoOCl_5]$ used in the following preparations were made by methods already detailed (J., 1927, 2145).

Dipyridinium Molybdenum Dioxytrithiocyanate.—10 C.c. of warm ammonium thiocyanate solution (containing 2·3 g.) were added to 30 c.c. of a warm, constantly stirred solution containing 4·5 g. of the salt $(C_5H_6N)_2[MoOCl_5]$. The bright reddish-brown crystals thus precipitated were washed with cold water and dried over phosphoric oxide in a vacuum. The compound melted at 181°, was soluble in acetone, and dissolved in boiling alcohol, giving a deep red solution.

Analysis. A hot ammoniacal solution of the substance was oxidised with hydrogen peroxide, and the molybdenum precipitated as sulphide (J., 1924, **125**, 1911), ignited, and weighed as the trioxide. The thiocyanate radical was determined by precipitation as silver thiocyanate from a cold, very dilute solution of the complex salt acidified with nitric acid. Nitrogen was estimated by Dumas's method (Found: Mo, 20·8; CNS, 37·6; N, 15·1; C, 33·9; H, 3·0. Calc. for $(C_5H_6N)_2[MoO_2(CNS)_3]$: Mo, 20·8; CNS, 37·7; N, 15·2; C, 33·8; H, 2·6%).

Diquinolinium Molybdenum Dioxytrithiocyanate.—25 C.c. of a solution containing 5·6 g. of the salt $(C_9H_8N)_2[MoOCl_5],H_2O$ were slowly poured with constant stirring into 15 c.c. of a warm, aqueous ammonium thiocyanate solution (containing 2·3 g.). This method gave a high yield of brownish-red crystals, which were washed and dried as previously described; they dissolved in boiling alcohol, but

were almost insoluble in water (Found: Mo, 17·1; CNS, 31·0; N, 12·5; C, 44·7; H, 3·36. Calc. for $(C_9H_8N)_2[MoO_2(CNS)_3]$: Mo, 17·1; CNS, 31·0; N, 12·5; C, 44·8; H, 2·85%).

Apart from their low solubility in water, the above-mentioned brownish-red complex thiocyanates $R_2[MoO_2(CNS)_3]$ closely resemble the copper-red pyridinium molybdenum dioxydichloride,

$$C_5H_6N[MoO_2Cl_2,H_2O],$$

previously described by the present authors (*loc. cit.*). Alcoholic hydrogen chloride converts all these red salts to the corresponding green complex chlorides $R_2[MoOCl_5]$, whilst on standing, their dilute aqueous solutions deposit light brown insoluble precipitates.

Treatment of $C_5H_6N[MoO_2Cl_2,H_2O]$ with ammonium thiocyanate, in an attempt to prepare $C_5H_6N[MoO_2(CNS)_2,H_2O]$, resulted in brownish-red crystals containing a high proportion of

$$(C_5H_6N)_2[MoO_2(CNS)_3].$$

Dihydrogen Molybdenum Dioxytrithiocyanate.—Hitherto no metallic salts of the type $R_2[MoO_2(CNS)_3]$ have been prepared. However, the addition of thallous or silver nitrate solution to a concentrated purple-red, aqueous solution of what is probably the complex acid $H_2[MoO_2(CNS)_3]$ gave rich purple precipitates. It proved extremely difficult to prepare pure specimens of these insoluble salts, owing to the simultaneous precipitation of thallous or silver thiocyanate, or even chloride. It seemed desirable, therefore, to find a method of preparing the acid, free from impurities, and also to attempt to determine its composition and constitution. The following method proved very satisfactory for the preparation of *dihydrogen molybdenum dioxytrithiocyanate*: To 15 c.c. of a solution of ammonium thiocyanate (4·6 g.) at 40° contained in a tap-funnel in an atmosphere of nitrogen, there were added 6·5 g. of the salt $(NH_4)_2[MoOCl_5]$, dissolved in 25 c.c. of warm water. The deep purple-red solution thus produced was agitated with 150 c.c. of ether, and the aqueous layer drawn off as completely as possible. About 2 c.c. of water were added to the ethereal extract remaining in the funnel, the mixture was agitated, and the aqueous layer completely withdrawn. By pressure of nitrogen, the ethereal solution was filtered into a flask which was evacuated to remove the ether. The product was a deep purple-red oil. The evacuated flask was heated on a water-bath, and the purple-red oil converted into an almost black solid which was kept in a vacuum over phosphoric oxide and solid potassium hydroxide (Found: Mo, 27·7; CNS, 52·5. Mo : CNS = 1 : 3·13. $H_2[MoO_2(CNS)_3],2H_2O$ requires Mo, 28·2; CNS, 51·2%). A solid of similar composition was obtained by keeping the oil for a long time over concentrated sulphuric acid.

In a modification of this method in which the flask containing the

solidified oil was connected with another flask containing concentrated sulphuric acid and the whole kept as highly evacuated as possible for a day, the solid *anhydrous acid* was obtained (Found : Mo, 31·2; CNS, 55·3; N, 14·3; Mo : CNS : N = 1 : 2·93 : 3·13. $H_2[MoO_2(CNS)_3]$ requires Mo, 31·6; CNS, 57·2; N, 13·8%).

Preparation of Dithallous Molybdenum Dioxytrithiocyanate.—The purple-red oil obtained as described above was mixed with 50 c.c. of water (the total volume of the mixture being *ca.* 55 c.c.), the solution warmed to 30°, and poured slowly with constant stirring into 50 c.c. of a saturated solution of thallous nitrate at 30°. The bluish-purple precipitate after being washed with water was dried in a vacuum over phosphoric oxide.

Analysis. To a weighed amount of the substance mixed with water, concentrated hydrochloric acid was added immediately with stirring, whereby the complex salt was partly decomposed with liberation of the free acid. The solution was now boiled to complete the decomposition of the salt. Some thallous chloride was precipitated, but with further dilution and boiling the precipitated chloride was wholly dissolved. To this boiling solution a slight excess of potassium iodide solution was added, and the precipitated thallium iodide was washed with very dilute potassium iodide solution, and finally with aqueous alcohol, and dried at 130—140°. The filtrate and washings were raised to boiling, treated with hydrogen peroxide, and the liberated iodine was boiled off. The resulting solution was made ammoniacal, boiled, and oxidised with more hydrogen peroxide until colourless, the molybdenum then being determined in the usual way (Found, for two samples : Mo, 13·4, 13·1; Tl, 55·9, 56·6; CNS, 24·0, 25·0; N, 6·0, 6·0. $Tl_2[MoO_2(CNS)_3,H_2O]$ requires Mo, 13·2; Tl, 56·0; CNS, 23·9; N, 5·8%).

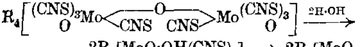
The composition of this *thallium* salt varied slightly with variations in the method of preparation. For example, it is essential to pour *the warmed purple-red solution of the complex acid into the thallium* nitrate solution, and not *vice versa.* Moreover, the preparation of the purple-red solution must be carefully carried out in order to avoid oxidation or contamination with thiocyanic or hydrochloric acid.

Salts of the Type $R_4[Mo_2O_3(CNS)_8]$.

The preparations of the three substituted ammonium molybdenyl pentachlorides used below are described later (p. 2737).

Tetra-trimethylammonium Dimolybdenum Trioxyoctathiocyanate.—A solution of 4 g. of $[(CH_3)_3NH]_2[MoOCl_5],H_2O$ in 10 c.c. of water was poured into 10 c.c. of a warm, constantly stirred, aqueous solution of ammonium thiocyanate (3·1 g.). The copious purple crystalline precipitate was washed with water and dried in a vacuum

over phosphoric oxide (Found: Mo, 20·3, 20·35; CNS, 49·1 N, 17·9; C, 25·2; H, 4·25. $[(CH_3)_3NH]_4[Mo_2O_3(CNS)_8]$ require Mo, 20·3; CNS, 49·2; N, 17·8; C, 25·4; H, 4·24%); it exhibits a green lustre and leaves a bluish-purple streak on unglazed porcelain It is sparingly soluble in cold water, but more soluble in hot, owing to hydrolysis. Concentrated solutions are purple, but on dilution turn blood-red, then orange, and finally bright yellow. An interesting reaction of this complex thiocyanate is its decomposition with thallous nitrate: To a warm, blood-red, saturated solution of the octathiocyanate, there was added, drop by drop, a saturated aqueous solution of thallous nitrate. A purple or reddish-purple precipitate was obtained if care was taken to add insufficient thallous nitrate for complete precipitation, which was shown by the supernatant liquid remaining reddish-orange. After washing and drying in a vacuum over phosphoric oxide, this precipitate gave Mo, 12·8; Tl 58·1; CNS, 24·1; Tl:CNS = 2 : 2·93, showing it to be an impure specimen of $Tl_2[MoO_2(CNS)_3,H_2O]$. The isolation of this thallium derivative indicates that the octathiocyanate undergoes hydrolysis in solution in such a way as to indicate a symmetrical structure for the octathiocyanate



$$2R_2[MoO{\cdot}OH(CNS)_4] \longrightarrow 2R_2[MoO_2(CNS)_3] + 2HCNS.$$

The action of thiocyanic acid on the octathiocyanate furnishes additional evidence in favour of the above configuration.

Tetra-tetramethylammonium Dimolybdenum Trioxyoctathiocyanate.—Into 10 c.c. of a warm aqueous solution of ammonium thiocyanate (2·8 g.), there were slowly poured with constant stirring 10 c.c. of a solution containing 4 g. of $[(CH_3)_4N]_2MoOCl_5$. An excellent yield of a magenta salt was obtained, which was washed with water and dried in a vacuum over phosphoric oxide (Found: Mo, 19·3; CNS, 46·6; N, 16·9; C, 28·7; H, 4·92. $[(CH_3)_4N]_4[Mo_2O_3(CNS)_8]$ requires Mo, 19·2; CNS, 46·5; N, 16·8; C, 28·8; H, 4·80%). On standing, the filtrate deposited bluish-purple crystals, exhibiting a green lustre, which had the same empirical composition as the first yield (Found: Mo, 19·25; CNS, 46·6; N, 16·6%). The properties of this second complex octathiocyanate resemble those of the trimethylammonium analogue.

In order to determine whether a similar octathiocyanate could be obtained with the diethylammonium derivative, the salt $[(C_2H_5)_2NH_2]_2MoOCl_5$ was prepared, and its reaction with ammonium thiocyanate studied. It was found that an oil resulted from which no crystalline substance could be isolated.

Tetrapyridinium Dimolybdenum Trioxysulphatohexathiocyanate.—By treating the reddish-brown thiocyanate, previously formulated as $(C_5H_5N)_2Mo(OH)_2(CNS)_3$, with sulphuric acid, Sand and Burger (*loc. cit.*) obtained from the resulting deep purple-red solution dark green needles, to which they assigned the formula

$$Mo(OH)(SO_4)_{\frac{1}{2}}(CNS)_3(C_5H_5N)_2,$$

basing their deductions on the following analysis:

	Mo.	N.	Total S.	S as SO_4.
Calc.	*19·47*	*14·19*	*22·72*	*3·25*
Found	19·17	13·66	23·01	3·01

By repeating this experiment, with slight modifications, we have isolated a purple compound which appears to have the configuration

$$(C_5H_6N)_4\left[\overset{(CNS)_3}{\underset{O}{}}Mo{<}^{O}_{SO_4}{>}Mo\overset{(CNS)_3}{\underset{O}{}}\right]$$

in which a relationship to the octathiocyanates

$$R_4\left[\overset{(CNS)_3}{\underset{O}{}}Mo{<}^{\quad O \quad}_{CNS\ CNS}{>}Mo\overset{(CNS)_3}{\underset{O}{}}\right]$$

is readily apparent. Although the colour of this substance differs from that of the salt obtained by Sand and Burger, the two compounds are probably identical, for the analytical figures obtained by Sand and Burger for their substance agree very closely with those demanded by the formula ascribed to the purple compound.

Preparation. 9·0 G. of $(C_5H_6N)_2[MoOCl_5]$ in 40 c.c. of water were added to 25 c.c. of a warm solution containing ammonium thiocyanate (4·6 g.), and the precipitated thiocyanate

$$(C_5H_6N)_2[MoO_2(CNS)_3]$$

was dried, finely powdered, and treated with 150 c.c. of sulphuric acid (5*N*). On warming, a deep red solution resulted, and crystals gradually appeared on the surface of the liquid. Further warming caused the crystals to revert to a black oil, which later began to bubble. At this stage the well-shaken mixture was rapidly filtered, and the filtrate cooled, finally by ice-cold water. The crystals obtained were washed with sulphuric acid (5*N*), then with absolute alcohol, and finally dried in a vacuum over calcium chloride (Found: Mo, 19·1; CNS, 35·0; N, 13·9; SO_4, 9·72; C, 31·1; H, 2·50. Calc. for $(C_5H_6N)_4[Mo_2O_3(SO_4)(CNS)_6]$: Mo, 19·1; CNS, 34·7; N, 13·9; SO_4, 9·56; C, 31·1; H, 2·39%).

Properties. The bright purple crystalline compound was almost insoluble in alcohol, and sparingly soluble in cold water, but on continued contact the crystals slowly dissolved, producing a brown solution changing to yellow on dilution. If the action of sulphuric acid was continued beyond the stage specified above, dark brown,

crystalline substances were produced (Found: Mo : N = 1 : 9 and Mo : CNS : N = 1 : 2 : 4). It appears probable that in these compounds some of the thiocyanate groups in the original purple salt have been replaced by sulphate equivalents.

Inconclusive results were obtained from the action of hydrochloric acid on $(C_5H_6N)_2[MoO_2(CNS)_3]$ and of sulphuric and hydrochloric acids on $(C_9H_8N)_2[MoO_2(CNS)_3]$.

Salts of the Type $R_2[MoO(CNS)_5]$.

Thiocyanic Acid Solution.—To 200 c.c. of a well-cooled solution of potassium thiocyanate (100 g.), 180 c.c. of sulphuric acid (5*N*) were slowly added with constant stirring, and the mixture was distilled in a vacuum, the distillate (*ca.* 200 c.c.) being collected in a well-cooled receiver. As a yellow substance separates on standing or prolonged boiling, freshly distilled acid was used in the following experiments.

Dipyridinium Molybdenyl Pentathiocyanate.—Dipyridinium molybdenum dioxytrithiocyanate (4·0 g.) was added to 150 c.c. of boiling thiocyanic acid, the solution rapidly filtered, and the filtrate cooled in ice. The crystals obtained were washed with cold thiocyanic acid solution, and dried in a vacuum over solid potassium hydroxide and phosphoric oxide. The compound was greenish-black in colour, and made a red mark on unglazed porcelain (Found: Mo, 17·1; CNS, 51·7; N, 17·4; C, 31·8; H, 2·28. $(C_5H_6N)_2[MoO(CNS)_5]$ requires Mo, 17·1; CNS, 51·7; N, 17·4; C, 32·0; H, 2·14%).

Diquinolinium Molybdenyl Pentathiocyanate.—This was prepared as above from the corresponding diquinolinium salt (5·0 g.) and thiocyanic acid (180 c.c.), greenish-black crystals being obtained (Found: Mo, 14·5; N, 14·9; C, 41·7; H, 2·49.

$(C_9H_8N)_2[MoO(CNS)_5]$

requires Mo, 14·5; N, 14·8; C, 41·7; H, 2·42%).

Ditrimethylammonium Molybdenyl Pentathiocyanate.—Tetratrimethylammonium dimolybdenum trioxyoctathiocyanate, prepared from 4 g. of $[(CH_3)_3NH]_2[MoOCl_5],H_2O$, was treated as before with 5 c.c. of thiocyanic acid solution and yielded greenish-black crystals of the required *compound* (Found: Mo, 18·5; CNS, 55·7; N, 18·8; C, 25·1; H, 4·03. $[(CH_3)_3NH]_2[MoO(CNS)_5]$ requires Mo, 18·4; CNS, 55·6; N, 18·8; C, 25·25; H, 3·83%).

Ditetramethylammonium Molybdenyl Pentathiocyanate.—3·0 G. of $[(CH_3)_4N]_2MoOCl_5$ were converted into the octathiocyanate. The finely powdered product was treated with thiocyanic acid (100 c.c.), whereupon reddish-brown crystals separated, which were very sparingly soluble in water, but more soluble in alcohol and chloroform (Found: Mo, 16·96; N, 17·34; C, 27·75; H, 4·59.

$[(CH_3)_4N]_2[MoO(CNS)_5],H_2O$

requires Mo, 16·89; N, 17·26; C, 27·45; H, 4·58%). Treatment with aqueous alcohol gave a magenta-coloured precipitate, which was probably the octathiocyanate regenerated by hydrolysis.

Salts of the Type $R_2[MoOCl_5]$.

For the preparation and investigation of the octathiocyanates previously described, the following complex molybdenyl pentachlorides were required. The preparations detailed below, involving electrolytic reduction and the use of alcoholic hydrogen chloride, differ from the method employed by Nordenskjold (*Ber.*, 1901, **34**, 1572), and give high yields of the pure salt.

Ditrimethylammonium Molybdenyl Pentachloride.—This salt was prepared by an alternative method to that previously described (J., 1927, 2148). To 100 c.c. of a boiling solution of quinquevalent molybdenum (10 g. Mo) in alcoholic hydrogen chloride, obtained as described under dipyridinium molybdenyl pentachloride (*loc. cit.*), there was added trimethylammonium chloride (16 g.). The well-stirred mixture was boiled until clear, and yielded yellowish-green needles, which were recrystallised from alcoholic hydrogen chloride and dried over potassium hydroxide and phosphoric oxide in a vacuum (Found: Mo, 22·6; Cl, 41·7; N, 6·59; C, 17·0; H, 5·10. Calc. for $[(CH_3)_3NH]_2[MoOCl_5],H_2O$: Mo, 22·5; Cl, 41·5; N, 6·56; C, 16·9; H, 5·15%).

Bisdiethylammonium Molybdenyl Pentachloride.—This was prepared as detailed above, except that diethylamine (13 g.) was used, the resulting solution being evaporated under diminished pressure. On re-saturation with hydrogen chloride, a large yield of green needles was obtained; these were washed with alcoholic hydrogen chloride and dried as before (Found: Mo, 21·9; Cl, 40·5; N, 6·40; C, 21·9; H, 5·65. $[(C_2H_5)_2NH_2]_2[MoOCl_5]$ requires Mo, 22·0; Cl, 40·5; N, 6·20; C, 22·0; H, 5·49%).

Ditetramethylammonium Molybdenyl Pentachloride.—An interesting point in connexion with the preparation of this salt is that by a variation in the proportions of the reactants it is possible to isolate a salt of the type $R[MoOCl_4,H_2O]$, of which so far only one other example is known, *viz.*, $(CH_3)_3NH[MoOCl_4,H_2O]$, previously described by the present authors. 50 C.c. of an alcoholic hydrogen chloride solution of quinquevalent molybdenum (6·4 g.) were diluted with an equal volume of alcohol, raised to boiling, and tetramethylammonium chloride (10 g.) added. The resulting light green crystals were dissolved in 200 c.c. of hydrochloric acid (4*N*), the solution saturated with hydrogen chloride, and on evaporation and re-saturation with this gas, crops of crystals were obtained. The first yields consisted of the *pentachloride*, whilst the last fraction proved

to be pure *monotetramethylammonium molybdenyl tetrachloride.* The salts were recrystallised, if necessary, and dried as previously described (Found, for pentachloride: Mo, 21·9; Cl, 40·4; N, 6·4. $[(CH_3)_4N]_2MoOCl_5$ requires Mo, 22·0; Cl, 40·5; N, 6·4%. Found, for tetrachloride: Mo, 27·70, 27·60; Cl, 41·15, 41·31; N, 4·04. $(CH_3)_4N[MoOCl_4,H_2O]$ requires Mo, 27·76; Cl, 41·0; N, 4·05%).

Physico-chemical Measurements.

Throughout this communication the various complex salts have been formulated in accordance with the principles of Werner's co-ordination theory. Indirect evidence for such a formulation is obtained from the method of preparation of the salts and from their reactions, but confirmation may be obtained from determinations of molecular weights and molecular conductivities. The slight solubility of the complex salts in cold water, and their decomposition by hot water, renders determinations of molecular weight unsatisfactory by either cryoscopic or ebullioscopic methods in air-free water. However, molecular conductivities were determined at 25°:

	$(C_5H_6N)_2[MoO_2(CNS)_3]$.				$(C_9H_8N)_2[MoO_2(CNS)_3]$.		
v	262·8	525·6	1051	2102	1090	2180	4360
μ	492	534	559	591	571	604	640

	$[(CH_3)_3NH]_4[Mo_2O_3(CNS)_8]$.				$[(CH_3)_4N]_4[Mo_2O_3(CNS)_8]$.			
v	736·3	2945	5890	11,781	882·6	3530	7061	14,122
μ	1614	1860	1900	1960	1711	1871	1942	2036

	$(C_5H_6N)_4[Mo_2O_3(SO_4)(CNS)_6]$.				
v	623·9	1248	2496	4991	9982
μ	1504	1713	1820	1930	2010

	$(C_5H_6N)_2[MoO(CNS)_5]$.				$[(CH_3)_3NH]_2[MoO(CNS)_5]$.			
v	441	1764	3529	7058	422	1688	3376	6752
μ	1089	1286	1314	1360	1069	1272	1305	1324

It is clear from the appended figures that in no case do the complex salts behave in aqueous solution as typical electrolytes, but exhibit abnormally high molecular conductivities. Such behaviour is not unexpected in view of the series of colour changes which aqueous solutions of the salts undergo with increasing dilution. According to our views on hydrolysis and ionisation, at infinite dilution salts of the type $R_2[MoO_2(CNS)_3]$ should give undissociated $[MoO_2OH,2H_2O]$ together with six ions, *viz.*, $2R^{\cdot} + H^{\cdot} + 3CNS'$. The ionic velocities at 25° are $H^{\cdot} = 347$; $CNS' = 65·4$ (Landolt–Börnstein, "Tabellen," 1923, ii, 1104); $C_5H_6N^{\cdot} = 43·1$ (Lundén, *J. Chim. physique*, 1907, **5**, 592); $C_9H_8N^{\cdot} = 35·1$; $(CH_3)_3NH^{\cdot} = 47·0$; $(CH_3)_4N^{\cdot} = 43·6$ (Bredig, *Z. physikal. Chem.*, 1894, **13**, 228). If the proposed scheme is correct the pyridinium

salt should give a value for $\mu_{\infty}^{25^{\circ}}$ of 629, which is in good agreement with the experimental values. It is interesting to find that Sand and Burger, in determining the molecular conductivity of this salt, obtained $\mu = 564$ and 613 for $v = 700$ and 2803 respectively, and concluded that the substance behaved abnormally, although no explanation was advanced. A scheme for the ionisation and hydrolysis of salts of the type $R_2[MoO(CNS)_5]$, identical with that previously recorded for the complex salts $R_2[MoOCl_5]$ (*loc. cit.*), would result in the ions $2R^{\cdot} + 3H^{\cdot} + 5CNS'$ being present at infinite dilution in aqueous solution. This should give, for

$$(C_5H_6N)_2[MoO(CNS)_5]$$

$\mu_{\infty} = 1454$, and for $[(CH_3)_3NH]_2[MoO(CNS)_5]$ $\mu_{\infty} = 1462$. The close agreement between the experimental and theoretical values lends strong support to the view that the scheme of hydrolysis and ionisation is substantially correct. A similar scheme for the complex salts of the new type $R_4[Mo_2O_3(CNS)_8]$ would be $R_4[Mo_2O_3(CNS)_8] + H_2O = 2R_2[MoO_2(CNS)_3] + 2HCNS$, followed by the further hydrolysis and ionisation of the complex salt as before, whence there should result at infinite dilution the ions $4R^{\cdot} + 4H^{\cdot} + 8CNS'$. Where $R^{\cdot} = (CH_3)_3NH^{\cdot}$, the calculated value for $\mu_{\infty} = 2099$, and where $R^{\cdot} = (CH_3)_4N^{\cdot}$, $\mu_{\infty} = 2086$ at 25°. Similarly, for the complex salt $(C_5H_6N)_4[Mo_2O_3(SO_4)(CNS)_6]$, the presence of the ions $4C_5H_6N^{\cdot} + 4H^{\cdot} + SO_4'' + 6CNS'$ in solution at 25° would give a calculated value for μ_{∞} of 2111. Again the agreement between the theoretical and experimental results is very satisfactory and therefore the formulation of these series of salts on the basis of the co-ordination theory seems to afford a satisfactory explanation of their behaviour in aqueous solution.

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THE UNIVERSITY OF BIRMINGHAM,
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CCCLXII.—*Attempted Resolution of Triethylenediaminenickel Chloride.*

By WILLIAM RALPH BUCKNALL and WILLIAM WARDLAW.

BY the resolution of the triethylenediamines of cobalt, chromium, rhodium, and iridium into their optically active antipodes, Werner (*Ber.*, 1912, **45**, 121, 865, 1228; *Helv. Chim. Acta*, 1920, **3**, 472)

advanced a brilliant proof of his theory that in these salts the associated ethylenediamine molecules are octahedrally distributed round the central metallic atom. Nevertheless, it is a matter of interest that the similarly constituted derivatives of bivalent metals such as copper, zinc, and nickel have so far remained unresolved. The idea that in these salts the units are distributed otherwise than octahedrally seems to be disproved by the X-ray evidence (Wyckoff, *J. Amer. Chem. Soc.*, 1922, **44**, 1239) that in salts such as $[Ni,6NH_3]Cl_2$ the units have the customary octahedral distribution. In view of this conclusion, and especially because there was no recorded attempt at the resolution of the complex salt $[Ni(en)_3]Cl_2$, the present research was undertaken, but with negative results.

For the resolution of triethylenediaminecobaltic chloride, Werner (*loc. cit.*) used the chloride- or bromide-tartrate, $[Co(en)_3]^{X}_{C_4H_4O_6}$, since he had found the normal tartrate unsuitable; and we therefore attempted to prepare the chloride-tartrate from $[Ni(en)_3]Cl_2$ by a similar method, *viz.*, the use of one equivalent of silver tartrate. It was found, however, that on crystallisation the solution gave rise to a mixture of the normal tartrate and the original chloride. Consequently, it was decided to attempt the fractional crystallisation of the normal *tartrate*, a solution of which was obtained by triturating a solution of the chloride with the theoretical amount of silver tartrate and repeatedly extracting the residue with hot water. On evaporation, the liquid became syrupy and the crystals which separated were difficult to filter. After several recrystallisations, no difference in rotatory power could be detected, although there seemed to be two tartrates present, one crystalline and the other a gel—the deep violet colour of the solution rendered accurate reading of small rotations difficult.

Although warm hydrobromic acid converts the tartrates of triethylenediaminecobalt into the bromides (Werner, *loc. cit.*), yet in the case of the nickel salt this acid effects a complete disruption of the complex ion, even in the cold, with the formation of nickel bromide and ethylenediamine hydrobromide; hence it appears that the nickel complex ion is less stable than its cobalt analogue. This disruption of the nickel salt was avoided by the addition of barium chloride solution in excess to a solution of the complex tartrate; the filtrate was then treated with alcohol to complete the precipitation of barium tartrate and examined in the polarimeter, but all fractions of the complex tartrate treated in this way were found to yield inactive solutions.

Since it was possible that tartaric acid was too weak an acid to

effect a good resolution (see Pope, J., 1899, **75**, 1105), the stronger acid, *d*-camphorsulphonic acid, was used. On crystallisation, the *triethylenediaminenickel* d-*camphorsulphonate* showed no tendency to form a gel, but after several recrystallisations, the difference in rotatory power between the first and last fractions was still too small to warrant the assumption that a resolution had been effected.

Thus it seems either that the rotatory power of the active nickel triethylenediamine is very small or that racemisation in solution is extremely rapid.

EXPERIMENTAL.

Preparation of Triethylenediaminenickel Chloride.—The method used was that of Werner and others (*Z. anorg. Chem.*, 1899, **21**, 201). Ethylenediamine hydrate (3 mols.) was added to a concentrated solution of pure crystallised nickel chloride (1 mol.), the solntion evaporated and crystallised, and the crystals twice recrystallised from water (Found: Ni, 16·85. Calc. for $[Ni(en)_3]Cl_2,2H_2O$: Ni, 16·95%).

Attempted Preparation of the Chloride–Tartrate.—A concentrated solution of the complex chloride (5 g.) was triturated with silver tartrate (2·5 g.), prepared from a concentrated solution of Rochelle salt by precipitation with concentrated silver nitrate solution, washing with water, and drying in a desiccator covered with black paper. The residue of silver chloride was repeatedly extracted with hot water and the extracts were filtered and evaporated. Different fractions of the deep violet crystals had nickel contents varying from 14·1 to 16·5%. Thus it is probable that the chloride–tartrate cannot be isolated and that the crystals obtained were mixtures of the tartrate and the chloride (Calc. for $[Ni(en)_3](C_4H_4O_6),2H_2O$; Ni, 13·8; for $[Ni(en)_3]_2{}^{Cl_2}_{(C_4H_4O_6)}$: Ni, 16·8%).

Preparation of Triethylenediaminenickel Tartrate.—A concentrated solution of triethylenediaminenickel chloride (4 g.) was triturated with silver tartrate (4 g.), and worked up as in the preceding case. The filtrate was very gel-like, rendering filtration difficult. Various fractions of crystals were dried on a porous plate, and all gave a constant nickel content (Found: Ni, 13·2; N, 19·3.

$$[Ni(en)_3](C_4H_4O_6),3H_2O$$

requires Ni, 13·3; N, 19·1%). Rotations of this substance were measured in a 0·5-dm. tube; after four recrystallisations the values of $[\alpha]_D$ for the first and last fractions were 17° and 21° respectively (α_D 0·11° and 0·15°). This difference is not greater than the probable experimental error. The tartrate was converted into the corresponding chloride by the method described above, but in each case the resulting solution was inactive.

Preparation of Triethylenediaminenickel d-*Camphorsulphonate*.—To 200 c.c. of a solution of silver nitrate (15 g.), just sufficient sodium hydroxide was added to precipitate all the silver as oxide; this was washed with distilled water until free from alkali salts, filtered, and the moist precipitate (11 g.) warmed with 150 c.c. of a solution of *d*-camphorsulphonic acid (20·5 g.). When dissolution of the oxide was complete, the filtered solution was neutral to litmus and contained 10 g. of the silver salt in 40 c.c. To 20 c.c. of a solution of recrystallised triethylenediaminenickel chloride (5 g.), 40 c.c. of the silver *d*-camphorsulphonate solution were added in small portions until the addition of one drop caused no more silver chloride to be precipitated; the solution was filtered, evaporated, and crystallised (Found: Ni, 8·15.

$$[Ni(en)_3](C_{10}H_{15}O_4S)_2,H_2O$$

requires Ni, 8·16%). The substance contained no chlorine. It was recrystallised several times from water, and rotations were measured for the mercury yellow line in a 0·5-dm. tube. No difference in rotation could be detected even after four recrystallisations, and [α] was constant at 17°.

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CCCLXIII.—*Complex Oxalates of Quinquevalent Molybdenum.*

By HENRY MILLS SPITTLE and WILLIAM WARDLAW.

SOME years ago Bailhache (*Bull. Soc. chim.*, 1903, **29**, 161; 1905, **33**, 439) prepared and investigated three crystalline complex oxalates of quinquevalent molybdenum, to which he assigned the formulæ $Mo_2O_2(OH)_6(C_2O_4)_2H_2Ba,H_2O$ and

$$Mo_2O_3(OH)_4(C_2O_3)_2(OH)_2R_2,2H_2O,$$

where R = K or NH_4. Such a formulation gives no indication of the relationship, structure, or reactions of these compounds, which therefore seemed to afford an opportunity for testing the value of Werner's co-ordination theory in elucidating the structure of chemical compounds, for by applying the principles of that theory, it was possible to consider these substances as members of a series

of the general formula $R[MoO_2(C_2O_4),xH_2O]$ where $R = K, (NH_4), \frac{1}{2}Ba$, etc.

In order to determine whether such a hypothesis was justifiable, and to investigate further the chemistry of molybdenum, we have prepared new members of the series, including the complex *acid* and *pyridinium* and *quinolinium* salts, and have submitted all these compounds to a physico-chemical examination.

EXPERIMENTAL.

In a previous communication (J., 1927, 2145) the preparation of salts of the type $R_2[MoOCl_5]$ was described. It has been found that when concentrated solutions of the pyridinium and quinolinium derivatives of this series are treated with oxalic acid, red solutions are obtained from which yellow solids separate. These substances have been shown to be complex oxalates. When the potassium and ammonium complex chlorides are similarly treated, red solutions are obtained, bnt owing to their high solubility, the resulting products are not precipitated.

Quinolinium Molybdenum Dioxyoxalate.—This new salt was prepared by adding 30 c.c. of a warm aqueous solution of oxalic acid (1·2 g.) to 30 c.c. of a solution containing 5·6 g. of $(C_9H_8N)_2[MoOCl_5],H_2O$, boiling the solution, filtering it hot, and cooling it; a bright yellowish-brown powder was thus obtained, which, after being washed with cold water and recrystallised from hot water, was dried in a vacuum over calcium chloride.

Analysis. The molybdenum was estimated by ignition of the compound to the trioxide, or by precipitation as trisulphide (J., 1924, **125**, 1911) and oxidation to trioxide, which was weighed. The nitrogen was determined by the method of Dumas, and the oxalate by the following process: To 200 c.c. of a boiling aqueous solution of the complex salt (0·3 g.), 5 c.c. of potassium hydroxide solution (20%) were added. The precipitated hydroxide was removed, and the colourless filtrate concentrated to about 30 c.c. One c.c. of nitric acid (5*N*) was now added, and after boiling for about 2 minutes, the solution was acidified with sulphuric acid and titrated with standard potassium permanganate {Found: Mo, 26·3; C_2O_4, 24·3; N, 3·9. $(C_9H_8N)[MoO_2(C_2O_4),H_2O]$ requires Mo, 26·4; C_2O_4, 24·2; N, 3·85%}.

The formation of tbis salt is in accordance with the scheme of hydrolysis and ionisation previously proposed (*loc. cit.*) for the complex chlorides $R_2[MoOCl_5]$.

Complex Pyridinium Molybdenum Oxyoxalates.—50 C.c. of a warm aqueous solution of oxalic acid (4·8 g.) were added to 50 c.c. of a solution of $(C_5H_6N)_2[MoOCl_5]$ (18·4 g.) and the mixture was heated.

There separated on cooling an orange-yellow powder, which was washed with cold water and dried in a vacuum over calcium chloride {Found: Mo, 31·6; C_2O_4, 29·0; N, 3·5; C, 22·6*; H, 2·5*; Mo : C_2O_4 : N : C : H = 4 : 4 : 3 : 23 : 30. $(C_5H_6N)_3H[Mo_4O_8(C_2O_4)_4,6H_2O]$ or $(C_5H_6N)_3[Mo_4O_7(OH)(C_2O_4)_4,6H_2O]$ requires Mo, 31·6; C_2O_4, 29·0; N, 3·5; C, 22·7; H, 2·6%; Mo : C_2O_4 : N : C : H = 4 : 4 : 3 : 23 : 31}. The presence of quinquevalent molybdenum in this compound was confirmed by a valency determination.

In an attempt to prepare a normal salt from the above pyridinium salt, 1—2 g. of this compound were gently boiled under reflux with about 20 c.c. of pyridine. After removal of the pyridine by decantation, the operation was repeated on the product, and after drying in a vacuum over concentrated sulphuric acid until free from pyridine, the final product was a pale yellow powder, soluble in water {Found: Mo, 25·4; C_2O_4, 23·3; N, 7·4. $(C_5H_6N)[MoO_2(C_2O_4),C_5H_5N]$ requires Mo, 25·6; C_2O_4, 23·5; N, 7·5%}. Valency determinations indicated that quinquevalent molybdenum was present.

Treatment of the quinolinium complex oxalate with quinoline did not result in the replacement of the water molecule owing to the oxidation of the molybdenum.

Barium Molybdenum Dioxyoxalate.—For the preparation of this compound (barium oxalomolybdite), Bailhache (*loc. cit.*) used two methods. The second method, which he considered preferable, involved the reduction of a hydrochloric acid solution of ammonium molybdate by red phosphorus, and addition of ammonium oxalate and barium chloride to the solution of quinquevalent molybdenum obtained. It was found, however, that this method yielded an impure salt containing a small amount of phosphate, and it was discarded in favour of the following method: 300 C.c. of an aqueous solution of oxalic acid (12 g.) were added to 300 c.c. of a solution of $(NH_4)_2[MoOCl_5]$ (35 g.) and the mixture was warmed. To the blood-red solution produced, barium chloride (11 g.) in 600 c.c. of water was added, and on heating to about 70°, a red, crystalline solid separated, which was collected hot, washed with hot water, and dried over calcium chloride in a vacuum {Found: Mo, 29·0; Ba, 20·8; C_2O_4, 26·6. Calc. for $Ba[MoO_2(C_2O_4)]_2,5H_2O$: Mo, 29·1; Ba, 20·8; C_2O_4, 26·7%}. An equally satisfactory product was obtained by use of the pyridinium and quinolinium derivatives of the series $R_2[MoOCl_5]$.

The very soluble ammonium and potassium and the less soluble pyridinium and quinolinium compounds can readily be prepared by double decomposition of this insoluble barium salt with the appropriate sulphate.

* Microanalysis.

Potassium Molybdenum Dioxyoxalate.—A satisfactory yield of this substance was obtained by the following method used by Bailhache, who, however, gave no experimental details. To 30 c.c. of a boiling aqueous solution of potassium sulphate (1·7 g.), barium molybdenum dioxyoxalate (7·0 g.) was added, and, after the mixture had been boiled for some minutes in a current of nitrogen, the insoluble sulphate was removed by filtration. If the filtrate was concentrated over phosphoric oxide at room temperature, tufts of golden needles were obtained, sometimes associated with red crystals. The yellow were separated from the red crystals by hand-picking and dried on a porous plate (Found: Mo, 30·3; C_2O_4, 27·8; K, 12·2. $K[MoO_2(C_2O_4),3{\cdot}5H_2O]$ requires Mo, 30·2; C_2O_4, 27·7; K, 12·3%).

The red crystals (Found: Mo, 32·0; C_2O_4, 29·3. Calc. for $K[MoO_2(C_2O_4),2{\cdot}5H_2O]$: Mo, 32·0; C_2O_4, 29·3%) proved to be the less hydrated compound analysed by Bailhache. This red form separates in a pure condition from a very concentrated solution of the potassium complex oxalate (prepared as described) which has been slowly cooled and inoculated with a red crystal.

By drying over sulphuric acid in a vacuum, either form loses water and produces a yellow powder of the empirical formula $K[MoO_2(C_2O_4),1{\cdot}5H_2O]$ (Found: Mo, 34·0; C_2O_4, 31·4. Calc.: Mo, 34·0; C_2O_4, 31·2%).

On concentration of a solution of any of these hydrated salts at 100° in a vacuum, a red solid results (Found: Mo, 35·4; Mo : C_2O_4 = 1·00 : 1·00. $K[MoO_2(C_2O_4),H_2O]$ requires Mo, 35·2%); this was formulated by Bailhache (*loc. cit.*) as $Mo_2O_5(C_2O_3)_2(OH)_2K_2$, which may be rewritten as $K[MoO_2(C_2O_4),0{\cdot}5H_2O]$. In no case, however, have the present anthors been able to obtain a substance with a lower water content than that demanded by

$$K[MoO_2(C_2O_4),H_2O].$$

Ammonium Molybdenum Dioxyoxalate.—This salt was prepared by double decomposition of ammonium sulphate (1·3 g.) and barium molybdenum dioxyoxalate (7·5 g.). The preparation should be carried out in an atmosphere of nitrogen, for an aqueous solution of this salt oxidises more readily than a solution of the potassium derivative. The salt in the form of tufts of golden needles could not be isolated in sufficient quantity for analysis. By methods similar to those described for the isolation of the red crystals of the potassium salt, there were obtained orange crystals of the empirical formula $(NH_4)[MoO_2(C_2O_4),2{\cdot}5H_2O]$ (Found: Mo, 34·4; C_2O_4, 31·6; NH_4, 6·5. Calc.: Mo, 34·4; C_2O_4, 31·5; NH_4, 6·5%). On drying this salt over sulphuric acid in a vacuum, a yellow powder was obtained (Found: Mo, 36·6; C_2O_4, 33·6; NH_4, 6·9. Calc. for

$(NH_4)[MoO_2(C_2O_4),1{\cdot}5H_2O]$: Mo, 36·8; C_2O_4, 33·7; NH_4, 6·9%). When a solution of this ammonium salt was evaporated to dryness in a vacuum at 100°, a brittle red crust was obtained similar in composition to the potassium analogue {Found: Mo, 38·0; Mo : C_2O_4 : NH_4 = 1·00 : 1·00 : 1·01. $(NH_4)[MoO_2(C_2O_4),H_2O]$ requires Mo, 38·1%}.

Quinolinium Molybdenum Dioxyoxalate.—Barium molybdenum dioxyoxalate (7·0 g.) was added to quinolinium sulphate (3·5 g.) dissolved in 60 c.c. of boiling water. After being boiled for some minutes in an atmosphere of nitrogen, the liquid was filtered hot, and the bright yellowish-brown crystals which separated were washed with cold water and dried in a vacuum over calcium chloride {Found: Mo, 26·2; C_2O_4, 24·2; N, 3·85; C, 35·7*; H, 2·65*. Calc. for $(C_9H_8N)[MoO_2(C_2O_4),H_2O]$: Mo, 26·4; C_2O_4, 24·2; N, 3·85; C, 36·3; H, 2·8%}.

Complex Pyridinium Molybdenum Oxyoxalates.—By analogy with the potassium, ammonium, and quinolinium salts, a pyridinium salt of the type $(C_5H_6N)[MoO_2(C_2O_4),xH_2O]$ should be formed by interaction of pyridininm sulphate with barium molybdenum dioxyoxalate. In the preparation of a pyridinium salt from the pyridinium complex chloride $(C_5H_6N)_2[MoOCl_5]$, however, a normal salt was not obtained (p. 2744). The following method yields a normal salt provided that the details are carefully observed. To 15 c.c. of boiling water, pyridinium sulphate (1·2 g.) and then barium molybdenum dioxyoxalate (3·5 g.) were quickly added. After boiling for 1 minute, the liquid was immediately filtered hot. The deep chrome-yellow powder, which separated from the filtrate on rapid cooling, was dried in a vacuum over calcium chloride {Found: Mo, 30·6; C_2O_4, 28·1; N, 4·4. $(C_5H_6N)[MoO_2(C_2O_4),H_2O]$ requires Mo, 30·6; C_2O_4, 28·0; N, 4·5%}.

This normal salt is rapidly decomposed on boiling with water, and a yellow solid of varying composition separates from the aqueous solution on cooling. If, however, the pyridine is removed from the reaction, the acid salt is formed in accordance with the equation

$$4(C_5H_6N)[MoO_2(C_2O_4),H_2O] + 2H_2O = (C_5H_6N)_3H[Mo_4O_8(C_2O_4)_4,6H_2O] + C_5H_5N.$$

For the preparation of this acid salt, the same reaction mixture that was used for the preparation of the normal salt was subjected to steam distillation in an atmosphere of nitrogen for about an hour to remove any liberated pyridine. The residual solution was filtered hot after concentration to about 10 c.c., and the orange-yellow powder which separated on cooling was washed with cold

* Microanalysis.

water and dried in a vacuum over calcium chloride {Found : Mo, 31·6; C_2O_4, 28·8; N, 3·5. Calc. for $(C_5H_6N)_3H[Mo_4O_8(C_2O_4)_4,6H_2O]$: Mo, 31·6; C_2O_4, 29·0; N, 3·5%}. It appears from the results of the above experiment that complex pyridinium salts with a ratio C_5H_5N : Mo of less than 3 : 4 do not exist.

In order to determine whether the molecule of water present in the normal salt could be replaced as in the case of the acid pyridinium salt, the normal salt was treated with pyridine as previously described. The product had the same empirical formula and properties as that obtained from the acid pyridinium salt {Found : Mo, 25·4; C_2O_4, 23·5; N, 7·5. Calc. for $(C_5H_6N)[MoO_2(C_2O_4)(C_5H_5N)]$: Mo, 25·6; C_2O_4, 23·5; N, 7·5%}.

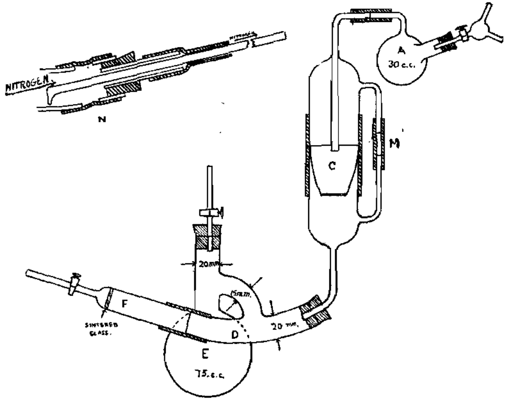
An Oxyoxalate of Quinquevalent Molybdenum.—The complex oxalates so far mentioned have been considered as derivatives of a hypothetical acid, $H[MoO_2(C_2O_4),xH_2O]$. Such an acid should be formed initially when the insoluble barium salt $Ba[MoO_2(C_2O_4)]_2,5H_2O$ is treated with dilute sulphuric acid. By warming this mixture a red supernatant liquid was obtained. Titrations with standard potassium permanganate, however, showed that in the solution the molybdenum was not quinquevalent, but had been partly oxidised. It was necessary, therefore, to conduct the whole preparation in an atmosphere from which air was rigidly excluded, and the following method proved satisfactory for the isolation of a substance with the empirical formula $Mo_2O_3(C_2O_4)_2,4H_2O$.

Into *A* (Fig. 1), which consisted of a 30 c.c. flask fitted with a side tube, were introduced barium molybdenum dioxyoxalate (4·0 g.) and water (7 c.c.). The whole apparatus was evacuated, tested to prove absence of air-leaks, and filled with nitrogen; 2 c.c. of sulphuric acid (5*N*) were then added to the liquid in *A*. With a slow stream of nitrogen passing through the apparatus from *F* to *A*, the reaction mixture was gradually raised to boiling point on a water-bath; this heating should occupy about an hour, for if the mixture is boiled quickly, hydrolysed products result. After gently boiling for 5 minutes, the red liquid formed was decanted into the filtering apparatus, *C*, by rotating the flask *A* : *C* consisted of a Gooch crucible, containing a perforated plate between two filter-papers, fitted into the modified adapter. By applying suction at *F*, the liquid was drawn into *C*, and by closing *M* it was filtered into *D*, which should hold about 12 c.c. of liquid. After this filtration, the apparatus was disconnected at *D*, the open end of *D* immediately closed with a solid rubber bung, and *DEF* evacuated. The liquid was concentrated at 30—35° to about 2 c.c. by means of the phosphoric oxide contained in the flask *E* of 75 c.c. capacity. Nitrogen was admitted into *DEF*, and from the liquid a bright

orange-yellow solid slowly separated. The mixture was then transferred to the filter *F*, by means of the device *N*, a rapid stream of nitrogen being passed through the apparatus to avoid oxidation. After the liquid had been filtered in nitrogen, the vessel *F* and its contents were rapidly transferred to a nitrogen-filled desiccator and dried over sulphuric acid in a vacuum.

The pale yellow substance thus obtained [Found: Mo, 39·4; C_2O_4, 36·3. $Mo_2O_3(C_2O_4)_2,4H_2O$ requires Mo, 39·4; C_2O_4, 36·1%], which corresponds to the parent *acid*, was insoluble in cold water

FIG. 1.



or in cold concentrated hydrochloric or nitric acid, and was stable in air. In hot water it dissolved with oxidation, and in warm hydrochloric acid a green solution was produced. Red solutions resulted from treatment with dilute ammonia or alkalis. Cold water in which the solid was suspended reacted acid. Valency determinations proved that the molybdenum was quinquevalent.

Valency of the Molybdenum.—In the presence of the oxalic acid the ordinary method (J., 1923, **123**, 969) for the determination of valency was not available, and estimations were therefore carried out by the following method. A weighed quantity of the substance, dissolved in air-free sulphuric acid (2*N*), was titrated in the cold in a nitrogen atmosphere with standard potassium permanganate. When colourless, the solution was heated to 70°, and the titration

continued until a permanent pink colour was obtained. This reading gave the amount of permanganate necessary to oxidise the molybdenum to the sexavalent state and to decompose the oxalate radical. The permanganate reqnired for the latter purpose was estimated independently by the method already described (p. 2743). By difference the amount of permanganate required to oxidise the molybdenum to the sexavalent condition was obtained, and since 1 c.c. of *N*-permanganate = 0·096 g. Mo^{v}, the percentage of molybdenum present in the salt can be deduced. When this agrees with the results obtained by gravimetric analysis, the molybdenum is *quinquevalent*.

Koppel and Goldmann (*Z. anorg. Chem.*, 1903, **36**, 281) have made an interesting observation with regard to the valency titrations for the quadrivalent vanadium oxyoxalates. They found that the amount of permanganate required was less than that demanded by theory, and observed that quadrivalent vanadium oxyoxalate could not be prepared; it therefore seems probable that this compound undergoes atmospheric oxidation in a similar manner to the analogous molybdenum oxyoxalate.

General Properties.—The complex oxalates in the dry condition are stable in air, but their aqueous solutions very slowly oxidise. Concentrated aqueous solutions are blood-red, but on dilution become brownish-yellow to yellow. The substances are insoluble in such organic solvents as alcohol, ether, and benzene. Concentrated hydrochloric acid decomposes the oxalates, yielding green solutions of the complex chlorides $R_2[MoOCl_5]$, and a green solution is also obtained by the action of concentrated sulphuric acid. A red solution results from the reaction between the complex oxalates and thiocyanic acid.

Physico-chemical Measurements.

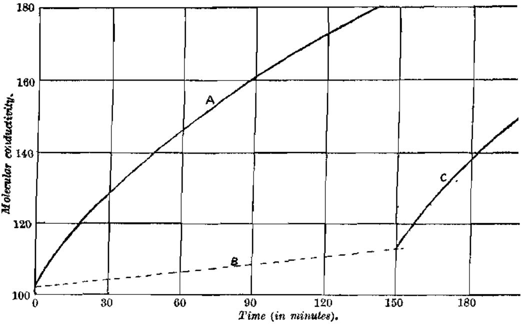
To decide whether formulæ based on Werner's co-ordination theory are applicable to these complex oxalates, determinations of their molecular weights and molecular conductivities were carried out.

Molecular-weight Determinations.—The molecular weights, as determined by the depression of the freezing point of air-free water, are shown in Table I. If the formula $K[MoO_2(C_2O_4),1{\cdot}5H_2O]$ is assigned to the potassium salt, the apparent molecular weight when ionisation is complete should be 141. The results obtained in dilute solution are in accordance with this deduction, but the apparent molecular weights in concentrated solutions, which are even greater than that demanded by the un-ionised molecule, indicate that polymerisation is taking place with the formation of such molecules as $K_2[Mo_2O_4(C_2O_4)_2,3H_2O]$. The fact that the

TABLE I.

G. of substance per 100 g. water.	Conc. (mols. per 1000 g. water).	Apparent mol. wt.	Osmotic factor.
Potassium molybdenum dioxyoxalate, $K[MoO_2(C_2O_4),1\cdot5H_2O]$.			
0·691	0·0245	171	1·65
0·862	0·0306	171	1·65
2·908	0·1031	209	1·35
4·180	0·1482	228	1·24
8·220	0·2914	283	1·00
10·180	0·3608	300	0·94
Ammonium molybdenum dioxyoxalate, $(NH_4)[MoO_2(C_2O_4),1\cdot5H_2O]$.			
0·497	0·0190	154	1·70
1·200	0·0460	169	1·54
2·521	0·0966	177	1·47
3·953	0·1514	202	1·29

FIG. 2.



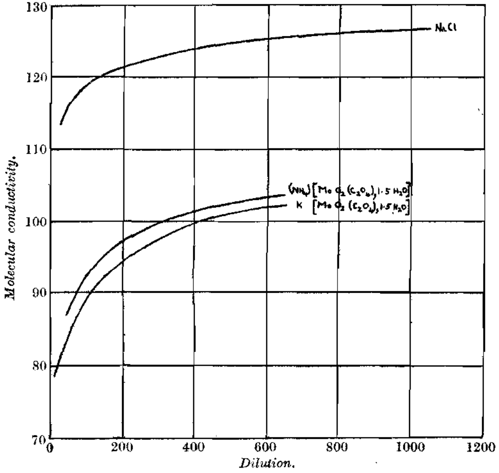
A. *Solution of* $K[MoO_2(C_2O_4),1\cdot5H_2O]$ *(830 litres/mol.) with platinised platinum electrodes.*
B. " " " (" " ") *without* " " "
C. *Solution B, on addition of platinised platinum electrodes.*

oxalate ion cannot be detected by its ionic reactions shows that the increased number of ions in dilute solutions is not due to hydrolysis of the complex anion.

Molecular-conductivity Determinations.—With solutions of the various complex oxalates, it was found that the molecular conductivity in each case increased with time, and that the rate of variation was greatest with dilute solutions. This change occurred extremely slowly in the absence of the platinised platinum electrodes, but was very markedly accelerated by their presence (Fig. 2). Similar observations were made by Duff (J., 1923, **123**, 572) on the catalytic hydrolysis of the cobaltammines, and by Russ (*Z. anorg.*

Chem., 1902, **31**, 42) on the catalytic oxidation of the complex niobium oxalates by platinised platinum electrodes. On treating an aqueous solution of potassium molybdenum dioxyoxalate with platinum-black, and estimating both valency and oxalate by means of standard potassium permanganate at intervals of several days, it was found that oxidation of the molybdenum to the sexavalent state took place and was accompanied by decolorisation of the solution.

FIG. 3.



It was therefore necessary to determine the conductivity by taking time curves for the conductivity at each dilution (see J., 1927, 515), and deducing the initial conductivities from these. Table II gives the values of μ for various dilutions (v litres per mol.) at 25° at zero time, and for comparison the values of molecular conductivities at 25° of typical salts (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 454) are given in Table III.

In dilute solutions the molecular conductivities are similar to those of a typical binary electrolyte (Fig. 3) and support the formulation $R[MoO_2(C_2O_4),xH_2O]$ for the molybdenum dioxyoxalates

Table II.

$K[MoO_2(C_2O_4),1{\cdot}5H_2O]$.

v	15·3	34·7	103·7	175·8	391·8	613·2
μ	79·3	81·6	89·4	92·4	99·4	101·6

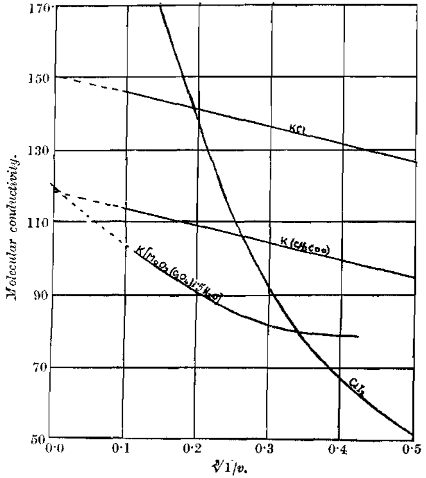
$(NH_4)[MoO_2(C_2O_4),1{\cdot}5H_2O]$.

v	54·4	77·8	178·2	271·3	618·0
μ	88·0	90·2	96·3	98·9	103·2

Table III.

v	20	50	100	200	500	1000	∞
NaCl	111·8	116·1	118·8	121·0	123·05	124·1	127
KCl	133·3	138·5	141·4	143·95	146·55	—	150·6

Fig. 4.



investigated above. The Ostwald–Walden rule does not apply in the case of these complex oxalates, for $\frac{1}{10}(\lambda_{1024} - \lambda_{32})$ has a value of approximately 2 for both salts. This may be due to the polymerisation that takes place in their concentrated solutions. Russ (*loc. cit.*) obtained similar results with the complex niobium oxalates. A further indication that these molybdenum dioxyoxalates behave abnormally is afforded by the graphs obtained by plotting $\sqrt[3]{1/v}$

against μ. Binary electrolytes in dilute solutions, unlike ternary electrolytes, give straight lines, but the complex oxalates give a curve (Fig. 4) agreeing with the idea that polymerisation to a more complex electrolyte takes place in solutions of higher concentration. Cadmium iodide, which is known to undergo extensive polymerisation in solution, is included for comparison.

Complex Pyridinium Molybdenum Oxyoxalate.—From the analytical data an empirical formula $(C_5H_6N)_3H[Mo_4O_8(C_2O_4)_4,6H_2O]$ or $(C_5H_6N)_3[Mo_4O_7(OH)(C_2O_4)_4,6H_2O]$ was assigned to this orange-yellow compound. It was impossible, however, without further data finally to decide as to the constitution of this salt, although the fact that in aqueous solution it reacts acid to litmus and bromophenol-blue favours the first formula. Determinations of molecular weight by the depression of the freezing point of water indicated that in dilute solutions considerable ionisation occurred—owing to the comparative insolubility of the compound it was possible to determine molecular weights and conductivities only over a limited range of concentrations :

G. of substance per 100 g. water.	Conc. (mols. per 1000 g. water).	Apparent mol. wt.	Osmotic factor.
0·506	0·00417	184	6·59
1·049	0·00864	195	6·22
1·684	0·01388	198	6·12

It is obvious from the results that, although primary ionisation may take place in accordance with the first formula, further decomposition of the complex anion must occur, for with such a formulation, the complex salt even at infinite dilution should yield a maximum of five ions by primary ionisation, and give an apparent molecular weight of 243, whereas the osmotic factor suggests that at least seven ions are present at the concentrations used. It may be inferred, therefore, that in all probability the complex anion undergoes decomposition, possibly in accordance with the following scheme :

$$(C_5H_6N)_3H[Mo_4O_8(C_2O_4)_4,6H_2O] \rightleftharpoons 3C_5H_6N^{\cdot} + H^{\cdot} + [Mo_4O_8(C_2O_4),6H_2O]''''$$

$$[Mo_4O_8(C_2O_4)_4,6H_2O]'''' \rightleftharpoons 4[MoO_2(C_2O_4),xH_2O]'.$$

Taylor (*Z. physikal. Chem.*, 1898, **27**, 361) obtained an osmotic factor of 5·92 for sodium mellitate, $Na_6C_{12}O_{12}$, in 0·00181*M* concentration.

If such a scheme operates, it should be possible to deduce the value of μ_∞ for this complex salt. Since μ_∞ for both $K[MoO_2(C_2O_4),1{\cdot}5H_2O]$ and $(NH_4)[MoO_2(C_2O_4),1{\cdot}5H_2O]$ is approximately 120, it follows that the ionic mobility of the complex ion

$[MoO_2(C_2O_4),xH_2O]'$ is approximately 46, the values of the ionic mobilities of the potassium and ammonium ions being 74·4 and 74·0 respectively at 25°. The possibility that there might be an error in the value of this ionic mobility due to the hydrolysis

$$R[MoO_2(C_2O_4),1{\cdot}5H_2O] + H_2O \rightleftharpoons ROH + H[MoO_2(C_2O_4),1{\cdot}5H_2O]$$

analogous to that of potassium cyanide, was disproved by the fact that the solutions of the complex oxalates, unlike those of potassium cyanide, do not give an alkaline reaction.

The above scheme indicates that μ_∞ for the complex pyridinium molybdenum oxyoxalate should be given by the sum of the ionic mobilities of $3C_5H_6N^{\cdot} + H^{\cdot} + 4[MoO_2(C_2O_4),xH_2O]'$, which is 660, whereas the following experimental data lead to a value of 570 :

v	65·13	151·6	196·9	719·9	2043·0
μ	419·7	452·8	464·5	503·1	521·0

Although no satisfactory explanation of the discrepancy between the two values for μ_∞ is apparent, it seems that an experimental value of this magnitude can only be explained by the supposition that a hydrogen ion is formed by this salt on solution, and that the constitution of this salt can be adequately expressed by the co-ordination formula $(C_5H_6N)_3H[Mo_4O_8(C_2O_4)_4,6H_2O]$. The graph (Fig. 5) obtained with the acid pyridinium salt when $\sqrt[3]{1/v}$ is plotted against μ is a straight line, but this may be accounted for by the very small range of concentrations over which the conductivities could be determined.

Discussion of Results.

Molybdenum oxyoxalate, $Mo_2O_3(C_2O_4)_2,4H_2O$, is an interesting example of a compound which is unstable and very reactive in solution, but far less reactive in the solid state, thus typifying the properties of polymerisable substances. Although from analytical data the above formula was assigned to this substance, yet a consideration of its markedly acidic properties and its method of preparation makes it clear that it is more adequately represented by the co-ordination formula $H[MoO_2(C_2O_4),1{\cdot}5H_2O]$. It thus becomes the parent acid of this series of complex oxalates.

With the exception of the acid pyridinium salt, the compounds of this series dealt with in this communication can be represented by the general formula $R[MoO_2(C_2O_4),xH_2O]$, where $x = 1, 1{\cdot}5, 2{\cdot}5$, or 3·5. Of these four groups of hydrates, the first appears to be the most general, and the suggestion that this is the normal one is strengthened by the fact that when the pyridinium salt

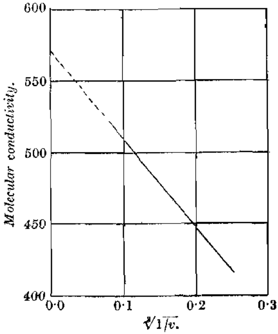
$$(C_5H_6N)[MoO_2(C_2O_4),H_2O]$$

is boiled with pyridine, a salt $(C_5H_6N)[MoO_2(C_2O_4),C_5H_5N]$, con-

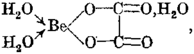
taining only one co-ordinated pyridine molecule, is produced. On Werner's theory these compounds apparently possess a co-ordination number of five, instead of the usual six for molybdenum compounds. This anomaly affords additional evidence for the theory of polymerisation put forward in the physicochemical section, for by considering two of the co-ordinating groups as bridge groups, the polymerised salts can be represented as six-point systems.

This theory of polymerisation is also needed to explain the existence of the acid pyridinium salt; moreover, it is necessary in the case of the higher hydrates, all of which can only be represented rationally by a formula which in the simplest case would be $R_2[Mo_2O_4(C_2O_4)_2.yH_2O]$, where $y = 3$, 5, or 7.

FIG. 5.



The large number of water molecules (5 or 7) in the higher hydrates of such a series is very difficult to explain, since the normal co-ordination number of six is exceeded. Such hydrated forms are only obtained in the crystalline state, and the extra molecules of water are only loosely held. Sidgwick (J., 1926, 1301) put forward a theory of the monohydration of the oxalate group both in the ionic and oxalato-form, in order to explain the existence of $Be(C_2O_4),3H_2O$, which he suggests is



, but this theory does not fully explain the hydrates of these complex oxalates.

Barbieri (*Rend. Atti Accad. Lincei*, 1916, 775) has described the preparation of another series of oxalates of quinquevalent molybdenum of the general formula $R_4[Mo_2O_4(C_2O_4)_3,2H_2O]$, where $R = K$ or NH_4. These have not been investigated in the present research, but it may be noted that they contain two molybdenum atoms and have a co-ordination number of six.

In his papers on the series of complex oxalates, Bailhache (*loc. cit.*) suggests for the potassium, ammonium, and barium salts the

name "oxalomolybdites," but it is felt that the use of the name "dioxyoxalates" would be more in accordance with modern nomenclature.

The authors wish to express their thanks to the Department of Scientific and Industrial Research for the award of a grant to one of them (H. M. S.), and to the Chemical Society and Messrs. Brunner Mond and Co., Ltd., for grants in aid of this investigation.

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CCCLXIV.—*The Interaction of Chloral and 2 : 4 : 6-Trihalogen-substituted Phenylhydrazines.*

By FREDERICK DANIEL CHATTAWAY and FRANCIS GEORGE DALDY.

IT has recently been shown (Chattaway and Bennett, J., 1927, 2850) that the violence of the reaction which occurs when chloral and phenylhydrazine are brought together is so moderated by the presence of halogen atoms in the hydrazine nucleus that the products, which differ according to the solvent in which the reaction takes place, can be isolated.

The reaction between chloral and the 2 : 4 : 6-trihalogen-substituted phenylhydrazines proceeds with such smoothness that its course can be completely followed. When chloral reacts with 2 : 4 : 6-trichlorophenylhydrazine, for example, it at first behaves normally, yielding a pale yellow hydrazone (I); this compound is extremely unstable and loses hydrogen chloride rapidly at the ordinary temperature, giving a compound (II) of a brilliant crimson colour which is indifferent to acetic anhydride and yields 2 : 4 : 6-trichloroaniline on reduction : it must therefore have an azo-structure and its composition shows it to be *αα-dichloro-β-2 : 4 : 6-trichlorobenzeneazoethylene*.

The elimination of hydrogen chloride from the initially formed hydrazone is a reversible reaction, for when a solution of the azo-compound (II) in hot acetic anhydride is saturated with hydrogen chloride, *chloral-α-acetyl-2 : 4 : 6-trichlorophenylhydrazone* is formed. The reaction may therefore be expressed :

$$NHX{\cdot}NH_2 + CCl_3{\cdot}CHO \longrightarrow \underset{\text{(I.)}}{[NHX{\cdot}N{:}CH{\cdot}CCl_3]} \rightleftharpoons \underset{\text{(II.)}}{NX{:}N{\cdot}CH{:}CCl_2} + HCl.$$

$$[X = C_6H_2Cl_3(2:4:6)].$$

Further evidence confirming the constitution of the crimson condensation product is afforded by the action of halogens upon it.

It combines with chlorine, for example, to give a yellow addition product (III), which from its colour must be regarded as having a hydrazone structure, the hydrogen atom previously attached to the methine carbon atom now being attached to the α-nitrogen atom. This compound, like the structurally analogous hydrazone (I), loses hydrogen chloride on warming with acetic acid or acetic anhydride, the colour reverting to crimson, since the azo-structure is re-established, the methine chlorine-substituted azo-compound, *ααβ-trichloro-β-2 : 4 : 6-trichlorobenzeneazoethylene* (IV), being formed.

$$\text{(III.)}\quad NHX\cdot N{:}CCl\cdot CCl_3 \longrightarrow NX{:}N\cdot CCl{:}CCl_2 + HCl \quad \text{(IV.)}$$

When the crimson compound (II) is heated with acetic acid containing hydrogen chloride, it is converted into *glyoxylic acid 2 : 4 : 6-trichlorophenylhydrazone*, and if it is heated with alcoholic hydrogen chloride, *ethyl glyoxylate 2 : 4 : 6-trichlorophenylhydrazone* is formed, the action in each case depending on the reversible nature of the elimination of hydrogen chloride from the 2 : 4 : 6-trichlorophenylhydrazone of chloral. This behaviour explains the formation of an alkyl glyoxylate 2 : 4 : 6-trichlorophenylhydrazone when chloral reacts with 2 : 4 : 6-trichlorophenylhydrazine in the corresponding alcohol.

The formation of the 2 : 4 : 6-trichlorophenylhydrazones of glyoxylic acid or the alkyl glyoxylates is due to the hydrolysis of the CCl_3 group of the chloralphenylhydrazone, but this is a much slower reaction than the elimination of hydrogen chloride; consequently, when the reaction between chloral and 2 : 4 : 6-trichlorophenylhydrazine takes place in acetic acid or alcoholic solution, there first occurs an almost complete formation of the azo-ethylene, which, as the hydrolysis proceeds, again combines with the hydrogen chloride.

When the reaction takes place in alcoholic solution, the reaction mixture turns brilliant crimson and the azo-ethylene can be isolated from it, but the colour gradually disappears as recombination with hydrogen chloride takes place and hydrolysis proceeds.

The formation of the glyoxylic acid and alkyl glyoxylate phenylhydrazones is therefore much facilitated by the presence of excess of hydrogen chloride during the reaction, which may be represented

$$NX{:}N\cdot CH{:}CCl_2 + HCl \rightleftharpoons NHX\cdot N{:}CH\cdot CCl_3 \xrightarrow{ROH} NHX\cdot N{:}CH\cdot CO_2R.$$

The action of halogens upon the 2 : 4 : 6-trichlorophenylhydrazones of glyoxylic acid or its esters yields the corresponding ω-halogenated hydrazones, which are also formed when the azo-compounds (IV)

are heated in presence of hydrogen chloride with acetic acid alcohol, respectively.

$$NHX{\cdot}N{:}CH{\cdot}CO_2R \xrightarrow{Cl_2} NHX{\cdot}N{:}CCl{\cdot}CO_2R \underset{HCl}{\overset{ROH}{\longleftarrow}} NX{:}N{\cdot}CCl{:}CCl_2.$$

ω-Halogenated alkyl glyoxylate 2 : 4 : 6-trichlorophenylhydrazo can also be obtained by esterification of the corresponding ω-halog ated glyoxylic acid 2 : 4 : 6-trichlorophenylhydrazones, and ve readily by the action of chlorine or bromine on *ethyl* 2 : 4 : 6- *chlorobenzeneazoacetoacetate*, prepared by coupling 2 : 4 : 6-t chlorobenzenediazonium chloride with ethyl acetoacetate (comp Bülow and Neber, *Ber.*, 1912, **45**, 3732); the acetyl group is remov and replaced by halogen; *e.g.*,

$$CH_3{\cdot}C(OH){:}\underset{CO_2Et}{CH} \xrightarrow{X{\cdot}N_2Cl} NHX{\cdot}N{:}\underset{CO_2Et}{C}{\cdot}CO{\cdot}CH_3 \xrightarrow{Cl_2} NHX{\cdot}N{:}\underset{CO_2]}{CCl}$$

The stability of the ω-halogenated 2 : 4 : 6-trichlorophen hydrazones of glyoxylic acid and its esters is remarkable: f instance, the halogen atom is not affected by boiling for a short tir with alcoholic ammonia, a process which readily yields a hydrazidi in the case of the ω-halogenated benzaldehyde- and *m*-nitrober aldehyde-2 : 4 : 6-trichlorophenylhydrazones.

EXPERIMENTAL.

When condensation of chloral and an arylhydrazine takes pla in aqueous solution, the azo-ethylene, being practically insolut in this solvent, separates and comparatively little hydrolysis occur but with acetic acid or alcohol as solvent, the azo-ethylene is fir formed, giving the reaction mixture an intense crimson colour, ar unless the hydrogen chloride is removed, hydrolysis occurs, th crimson colour disappears, and the hydrazone of glyoxylic acid its ester is formed. If, however, the acetic acid contains excess sodium acetate, recombination with hydrogen chloride and hydroly are prevented, and the azo-ethylene can be isolated.

Action of 2 : 4 : 6-Trichlorophenylhydrazine Hydrochloride Chloral Hydrate.—(1) *In aqueous solution.* Chloral hydrate (9 g 1 mol.) and 2 : 4 : 6-trichlorophenylhydrazine hydrochloride (13·5 g 1 mol.) were dissolved in 1000 c.c. of hot water containing 20 c. of hydrochloric acid, and the mixture was heated nearly to boilin As the temperature approached 80°, the liquid became turbid an *αα-dichloro-β-2 : 4 : 6-trichlorobenzeneazoethylene* separated in minu drops which coalesced to a viscid liquid of a brilliant crimson colou and solidified on cooling to a hard crimson cake. It crystallise from alcohol, in which it was very easily soluble, in deep crimso

acicular plates, m. p. 54° (Found : Cl, 58·05. $C_8H_3N_2Cl_5$ requires Cl, 58·25%).

(2) *In acetic acid solution in presence of sodium acetate.* The same quantities of reactants in 40 c.c. of acetic acid were warmed to 60°, the liquid turning deep crimson and hydrogen chloride being evolved; 8 g. (2 mols.) of finely powdered, anhydrous sodium acetate were then added, the mixture was heated on a water-bath for ½ hour, and the αα-dichloro-β-2 : 4 : 6-trichlorobenzeneazoethylene, which separated as a dark red liquid and solidified on cooling, was crystallised from alcohol.

(3) *In acetic acid solution.* If in the foregoing experiment, the mixture was heated to boiling without the addition of sodium acetate, after 10 minutes the colour had faded to orange, and on cooling, glyoxylic acid 2 : 4 : 6-trichlorophenylhydrazone separated. It crystallised from acetic acid, in which it was extremely soluble, in pale yellow, elongated plates, m. p. 167° (decomp.), identical with specimens prepared by direct synthesis.

(4) *In ethyl-alcoholic solution.* The hydrazine hydrochloride (12 g.; 1 mol.) was suspended in 50 c.c. of ethyl alcohol and 8 g. (1 mol.) of chloral hydrate were added; on being warmed for a few minutes, the solution turned crimson owing to the formation of the αα-dichloro-β-2 : 4 : 6-trichlorobenzeneazoethylene, for when a portion of the clear liquid was cooled, that compound separated. On further heating, the crimson colour slowly faded, and after an hour's boiling a clear yellow solution was obtained from which *ethyl glyoxylate 2 : 4 : 6-trichlorophenylhydrazone* separated on cooling. When crystallised from boiling alcohol, in which it was very soluble, it separated in pale yellow prisms, the colour deepening on exposure to daylight; m. p. 97·5° (Found : Cl, 36·1. $C_{10}H_9O_2N_2Cl_3$ requires Cl, 36·0%).

Reactions of αα-Dichloro-β-2 : 4 : 6-trichlorobenzeneazoethylene.—(1) *With alcohol.* 5 G. of the foregoing benzeneazoethylene were boiled with 25 c.c. of alcohol : after 8 hours, the crimson colour had changed to pale yellow, and on cooling, ethyl glyoxylate 2 : 4 : 6-trichlorophenylhydrazone separated. In a similar experiment in which the alcohol was first saturated with hydrogen chloride, the reaction was complete after 1 hour's boiling.

(2) *Formation of chloral-α-acetyl-2 : 4 : 6-trichlorophenylhydrazone.* A solution of 5 g. of αα-dichloro-β-2 : 4 : 6-trichlorobenzeneazoethylene in 10 c.c. of acetic anhydride was saturated at 80° with dry hydrogen chloride; the crimson colour faded rapidly, and on cooling, *chloral-α-acetyl-2 : 4 : 6-trichlorophenylhydrazone* separated as a colourless solid. It crystallised from boiling alcohol, in which it was readily soluble, in colourless rhombs, m. p. 144° (Found : N, 7·4; Cl, 55·25. $C_{10}H_8ON_2Cl_6$ requires N, 7·3; Cl, 55·5%).

(3) *Action of chlorine.* A stream of chlorine was passed into a well-cooled suspension of 10 g. of αα-dichloro-β-2 : 4 : 6-trichlorobenzeneazoethylene in 10 c.c. of acetic acid; the temperature rose slightly, and the solid dissolved, giving a pale orange solution from which *chloral-ω-chloro-2 : 4 : 6-trichlorophenylhydrazone* separated as a red, oily liquid; this solidified on standing with the mother liquor, and crystallised from boiling acetone, in which it was easily soluble, in small yellow prisms, m. p. 104° (Found: N, 7·2; Cl, 66·0. $C_8H_3N_2Cl_7$ requires N, 7·5; Cl, 66·2%).

If the pale orange solution was heated to boiling, hydrogen chloride was evolved and the crimson colour restored; on cooling, *ααβ-trichloro-β-2 : 4 : 6-trichlorobenzeneazoethylene* was deposited. It crystallised from alcohol, in which it was readily soluble, in long bright red needles, m. p. 75° (Found: Cl, 63·0. $C_8H_2N_2Cl_6$ requires Cl, 62·8%).

(4) *Action of bromine.* 2 C.c. (1 mol. + excess) of bromine dissolved in 5 c.c. of acetic acid were added to 5 g. (1 mol.) of αα-dichloro-β-2 : 4 : 6-trichlorobenzeneazoethylene suspended in 15 c.c. of acetic acid; the mixture was heated at 60° for 20 minutes and then cooled; the *αα-dichloro-α-bromo-β-2 : 4 : 6-trichlorobenzeneazoethylene* which separated crystallised from alcohol, in which it was easily soluble, in brick-red needles, m. p. 108·5° (Found: Cl, 46·1; Br, 20·7. $C_8H_2N_2Cl_5Br$ requires Cl, 46·2; Br, 20·75%).

Synthesis of Glyoxylic Acid and Ethyl Glyoxylate 2 : 4 : 6-Trichlorophenylhydrazones.—60 C.c. of 0·8*N*-glyoxylic acid solution (prepared by electro-reduction of oxalic acid) were added to 12 g. of 2 : 4 : 6-trichlorophenylhydrazine hydrochloride dissolved in 1000 c.c. of boiling water; *glyoxylic acid 2 : 4 : 6-trichlorophenylhydrazone* separated as a pale yellow, flocculent precipitate. It crystallised from hot acetic acid in pale yellow, elongated plates, m. p. 167° (decomp.) (Found: Cl, 39·7. $C_8H_5O_2N_2Cl_3$ requires Cl, 39·8%). When 5 g. of this compound were boiled for 6 hours with 25 c.c. of alcohol containing 2% of hydrogen chloride, and cooled, ethyl glyoxylate 2 : 4 : 6-trichlorophenylhydrazone separated as yellow prisms, m. p. 97·5°.

Ethyl Glyoxylate α-Acetyl-2 : 4 : 6-trichlorophenylhydrazone.—5 G. of ethyl glyoxylate 2 : 4 : 6-trichlorophenylhydrazone were dissolved in 10 c.c. of hot acetic anhydride and a drop of sulphuric acid was added; a violent reaction then set in. When the mixture was cooled, *ethyl glyoxylate α-acetyl-2 : 4 : 6-trichlorophenylhydrazone* separated. It crystallised from boiling alcohol, in which it was readily soluble, in colourless rhombs, m. p. 112·5° (Found: Cl, 31·6. $C_{12}H_{11}O_3N_2Cl_3$ requires Cl, 31·5%).

Action of Chlorine on Ethyl Glyoxylate 2 : 4 : 6-Trichlorophenyl-

hydrazone.—A stream of chlorine was passed into a suspension of 7 g. of ethyl glyoxylate 2 : 4 : 6-trichlorophenylhydrazone in 20 c.c. of acetic acid; the solid gradually dissolved and when a clear solution was obtained the whole was poured into water. *Ethyl glyoxylate ω-chloro-2 : 4 : 6-trichlorophenylhydrazone* immediately separated as a bulky, white solid; it crystallised from alcohol, in which it was easily soluble, in colourless plates, m. p. 73·5°, which turned pink on exposure to light (Found: Cl, 42·8. $C_{10}H_8O_2N_2Cl_4$ requires Cl, 43·0%).

This compound was also prepared by boiling a solution of 5 g. of αβ-trichloro-β-2 : 4 : 6-trichlorobenzeneazoethylene in 25 c.c. of alcohol for 8 hours; the crimson colour slowly faded to pale yellow, and on cooling, the required compound separated. In a similar experiment, the alcohol was first saturated with hydrogen chloride and the reaction was then completed in an hour.

Action of Bromine on Ethyl Glyoxylate 2 : 4 : 6-Trichlorophenylhydrazone.—2 C.c. (1 mol. + excess) of bromine were added to 5 g. (1 mol.) of the hydrazone dissolved in 25 c.c. of acetic acid, and the mixture was heated at 60° for ½ hour; on cooling, *ethyl glyoxylate ω-bromo-2 : 4 : 6-trichlorophenylhydrazone* separated. It crystallised from alcohol, in which it was extremely soluble, separating in feathery, white plates, m. p. 75° (Found: Cl, 28·6; Br, 21·5. $C_{10}H_8O_2N_2Cl_3Br$ requires Cl, 28·4; Br, 21·3%).

Action of Chlorine on Glyoxylic Acid 2 : 4 : 6-Trichlorophenylhydrazone.—A stream of chlorine was passed into a suspension of 10 g. of glyoxylic acid 2 : 4 : 6-trichlorophenylhydrazone in 30 c.c. of acetic acid: the temperature rose and the solid all dissolved, and on cooling, *glyoxylic acid ω-chloro-2 : 4 : 6-trichlorophenylhydrazone* separated. It crystallised from hot acetic acid in small yellow prisms, m. p. 151·5° (decomp.) (Found: Cl, 47·1. $C_8H_4O_2N_2Cl_4$ requires Cl, 47·0%).

5 G. of the foregoing compound were esterified by boiling for 6 hours with 25 c.c. of alcohol containing 2% of hydrogen chloride; when the resulting yellow solution was cooled, ethyl glyoxylate ω-chloro-2 : 4 : 6-trichlorophenylhydrazone separated as white plates, m. p. 73·5°, identical with the compound described above.

Ethyl 2 : 4 : 6-Trichlorobenzeneazoacetoacetate.—20 G. (1 mol.) of 2 : 4 : 6-trichloroaniline were diazotised and the filtered solution was added slowly and with vigorous stirring to a well-cooled mixture of 13 g. (1 mol.) of ethyl acetoacetate dissolved in 200 c.c. of alcohol and 300 g. of sodium acetate in 1500 c.c. of water. The *ethyl 2 : 4 : 6-trichlorobenzeneazoacetoacetate* that separated crystallised from alcohol in small yellow prisms, m. p. 94·5° (Found: Cl, 31·4. $C_{12}H_{11}O_3N_2Cl_3$ requires Cl, 31·5%).

Action of Chlorine and of Bromine on Ethyl 2 : 4 : 6-Trichloro benzeneazoacetoacetate.—When chlorine was passed into a suspension of 5 g. of the ester in 20 c.c. of acetic acid, heat was evolved; the pale yellow solution obtained, on cooling, deposited ethyl glyoxylate ω-chloro-2 : 4 : 6-trichlorophenylhydrazone as colourless plates m. p. 73·5°, identical with specimens previously prepared.

2 C.c. of bromine (1 mol. + excess) in 5 c.c. of acetic acid were added to 5 g. (1 mol.) of ethyl 2 : 4 : 6-trichlorobenzeneazoaceto-acetate in 20 c.c. of acetic acid and the mixture was heated at 60° for ½ hour: on cooling, ethyl glyoxylate ω-bromo-2 : 4 : 6-trichloro-phenylhydrazone separated in colourless needles, m. p. 75°, identical with the compound described above.

A similar series of reactions has been carried out with 2 : 4 : 6-tri-bromophenylhydrazine, and the following compounds prepared:—*αα-Dichloro-β-2 : 4 : 6-tribromobenzeneazoethylene*, crimson plates from alcohol, m. p. 92° (Found: C, 22·2; H, 0·9; N, 6·6; Cl, 16·2; Br, 54·7. $C_8H_3N_2Cl_2Br_3$ requires C, 21·9; H, 0·7; N, 6·4; Cl, 16·2; Br, 54·8%). *ααβ-Trichloro-β-2 : 4 : 6-tribromobenzeneazoethylene*, long, deep red, flat prisms from alcohol, m. p. 105° (Found: Cl, 22·4; Br, 50·6. $C_8H_2N_2Cl_3Br_3$ requires Cl, 22·5; Br, 50·8%). *αα-Dichloro-β-bromo-β-2 : 4 : 6-tribromobenzeneazoethylene*, flat, deep red prisms from alcohol, m. p. 115° (Found: Cl, 13·7; Br, 61·6. $C_8H_2N_2Cl_2Br_4$ requires Cl, 13·7; Br, 61·9%). *Glyoxylic acid 2 : 4 : 6-tribromophenylhydrazone*, faintly yellow, irregular plates from acetic acid, m. p. 170·5° (decomp.) (Found: Br, 59·6. $C_8H_5O_2N_2Br_3$ requires Br, 59·8%). *Ethyl glyoxylate 2 : 4 : 6-tri-bromophenylhydrazone*, pale yellow, flat prisms from alcohol, m. p. 126° (Found: C, 28·2; H, 2·1; N, 6·5; Br, 55·9. $C_{10}H_9O_2N_2Br_3$ requires C, 28·0; H, 2·1; N, 6·5; Br, 55·9%). *Ethyl glyoxylate α-acetyl-2 : 4 : 6-tribromophenylhydrazone*, colourless rhombs from alcohol, m. p. 133·5° (Found: C, 31·0; H, 2·4; N, 6·3; Br, 50·8. $C_{12}H_{11}O_3N_2Br_3$ requires C, 30·6; H, 2·4; N, 6·0; Br, 50·9%). *Ethyl glyoxylate ω-chloro-2 : 4 : 6-tribromophenylhydrazone*, colourless plates from alcohol, m. p. 108·5° (Found: Cl, 7·7; Br, 51·8. $C_{10}H_8O_2N_2ClBr_3$ requires Cl, 7·7; Br, 51·8%). *Ethyl glyoxylate ω-bromo-2 : 4 : 6-tribromophenylhydrazone*, elongated colourless plates from acetic acid, m. p. 102·5° (Found: Br, 62·8. $C_{10}H_8O_2N_2Br_4$ requires Br, 63·0%). *Ethyl 2 : 4 : 6-tribromobenzeneazoacetoacetate*, small yellow prisms from alcohol, m. p. 96·5° (Found: Br, 50·8. $C_{12}H_{11}O_3N_2Br_3$ requires Br, 50·9%).

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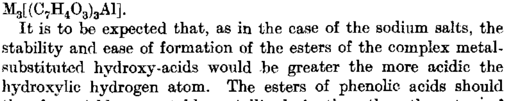
CCCLXV.—*Metallic Derivatives of Hydroxy-esters. Part I. Copper and Nickel Derivatives of Methyl Salicylate.*

By Brian Wilfred Doak and John Packer.

The alkali salts of the complex acids theoretically derived from hydroxy-acids by the replacement (in part at least) of the hydrogen of the hydroxyl groups by various metals have been the subject of many investigations (see Wark, J., 1923, **123**, 1816, 1826; 1924, **125**, 2004; 1927, 1753, for references). It is, however, impossible to assign definite constitutional formulæ to all but the simplest of them owing to the difficulty of distinguishing between the carboxylic and the hydroxylic hydrogen atom and the extent to which each is replaced by the metal of the complex anion.

The metallic derivatives of the corresponding hydroxy-esters appear to have been little investigated. The potassium and barium derivatives of methyl salicylate and various metallic derivatives of ethyl acetoacetate have long been known; sodium and potassium metalloacetoacetates, however, are unknown. Since the completion of the present work Burrows and Wark (this vol., p. 222) have described anhydrous methyl aluminosalicylate, $Al(C_8H_7O_3)_3$, the complex aluminosalicylic acid, $H_2\left[(C_7H_4O_3)_2Al{OH \atop OH_2}\right]$, and a number of its salts: they did not succeed in preparing salts of the type $M_3[(C_7H_4O_3)_3Al]$.

It is to be expected that, as in the case of the sodium salts, the stability and ease of formation of the esters of the complex metal-substituted hydroxy-acids would be greater the more acidic the hydroxylic hydrogen atom. The esters of phenolic acids should therefore yield more stable metallic derivatives than the esters of aliphatic hydroxy-acids, and for this reason salicylic acid was chosen for investigation first. Sodium cuprisalicylate (anhydrous) has been isolated by Wark (J., 1927, 1753), who assigns to it the formula $Na_2[Cu(C_7H_4O_3)_2]$.



(I.) (II.) (III.)

Starting with methyl salicylate, the authors have prepared ***methyl cuprisalicylate*** and ***nickelosalicylate*** as crystalline dihydrates, and *anhydrous* methyl cuprisalicylate, which differs somewhat from the

hydrated form in its solubility in organic solvents. The constitutions of the hydrates are best represented as in (I; X = Cu or Ni), the two molecules of water being held by co-ordination bonds to the central copper or nickel atom, which has a co-ordination number of four. These hydrates are non-volatile solids, undergoing exothermic decomposition on heating and leaving a quantitative residue of the metallic oxide. In this respect methyl cuprisalicylate dihydrate differs from ethyl cupriacetoacetate, which is not hydrated, is volatile below its decomposition temperature, and shows considerable solubility in liquids of low dielectric constant, such as chloroform, and therefore probably is a co-ordinated copper compound possessing a chelate ring structure as shown in (II), the dotted lines denoting co-ordination bonds (the copper atom sharing a pair of electrons belonging to each carbonyl oxygen atom and thus completing its octet of electrons). The tendency of anhydrous methyl cuprisalicylate towards similar co-ordination with chelate ring formation (III) is apparently small, as shown by its relatively small, although appreciable, solubility in chloroform (in which the hydrate is, however, insoluble) and its non-volatility.

Methyl cuprisalicylate and nickelosalicylate dihydrates are completely decomposed by mineral acids. They are insoluble in cold water; but when boiled with water, methyl cuprisalicylate undergoes complete hydrolysis to methyl salicylate and copper hydroxide (or oxide), and methyl nickelosalicylate yields methyl salicylate and *methyl hydroxynickelosalicylate* (IV: X = Ni; R = H). The

$$\text{(IV)}\ CO_2Me{\cdot}C_6H_4{\cdot}O{\cdot}X{\cdot}OR$$

$$\text{(V)}\ CO_2Me{\cdot}C_6H_4{\cdot}O{\cdot}Cu{\cdot}O{\cdot}Cu{\cdot}O{\cdot}C_6H_4{\cdot}CO_2Me$$

corresponding copper compound (IV: X = Cu; R = H) can be obtained, by less energetic hydrolysis, by passing wet air over methyl cuprisalicylate dihydrate at 100°. This *methyl hydroxycuprisalicylate*, on heating at 100° in a stream of dry air, undergoes dehydration to yield the *basic compound* (V). The hydrolysis of methyl cuprisalicylate, which occurs according to the equation

$$(CO_2Me{\cdot}C_6H_4{\cdot}O)_2Cu + H_2O \rightleftharpoons CO_2Me{\cdot}C_6H_4{\cdot}OH + CO_2Me{\cdot}C_6H_4{\cdot}O{\cdot}Cu{\cdot}OH,$$

is reversible, the hydroxycuprisalicylate slowly absorbing methyl salicylate vapour at the ordinary temperature. That hydrolysis can also proceed very slowly at the ordinary temperature is shown by the facts that methyl cuprisalicylate dihydrate gradually loses weight in a vacuum (2 cm.) to an extent greatly in excess of that corresponding to the loss of its two molecules of water and that methyl cuprisalicylate and nickelosalicylate dihydrates smell quite strongly of methyl salicylate at the ordinary temperature. An-

hydrous methyl cuprisalicylate, however, is stable at temperatures up to 100° in the absence of water vapour.

Methyl cuprisalicylate and nickelosalicylate dihydrates also undergo alcoholysis with methyl and ethyl alcohols. The reaction between methyl cuprisalicylate dihydrate and methyl alcohol occurs (partly at least) at the ordinary temperature, whereas that with ethyl alcohol occurs only on boiling. When boiled with methyl alcohol, both esters yield the respective *methoxymetallo-salicylates* (IV: X = Cu or Ni; R = Me) as insoluble residues. The reaction

$$(CO_2Me\cdot C_6H_4\cdot O)_2X + MeOH \rightleftharpoons CO_2Me\cdot C_6H_4\cdot OH + CO_2Me\cdot C_6H_4\cdot O\cdot X\cdot OMe$$

is reversible and the insoluble methoxy-compound can readily be made to pass into methyl-alcoholic or acetone solution as the original metallosalicylate by the addition of methyl salicylate. The reversibility of this reaction is the basis of the method for the preparation of anhydrous methyl cuprisalicylate (see p. 2768).

On boiling with ethyl alcohol, methyl nickelosalicylate dihydrate gives the corresponding insoluble *ethoxy-compound* (IV: X = Ni; R = Et). Methyl cuprisalicylate dihydrate behaves differently, the alcoholysis with boiling ethyl alcohol proceeding a stage further to give small quantities of methyl salicylate and *cupric ethoxide*, $Cu(OEt)_2$. The addition of very little methyl salicylate completely suppresses the alcoholysis in this case.

These alkyloxy-derivatives are stable in the absence of moisture, even at 100°, but undergo hydrolysis in its presence, although only very slowly at the ordinary temperature. Methyl methoxycupri-salicylate, on heating at 100° in a stream of moist air, gives methyl alcohol and the same hydroxycuprisalicylate as is obtained by the hydrolysis of the original cuprisalicylate.

Direct methylation of sodium cuprisalicylate, $Cu(O\cdot C_6H_4\cdot CO_2Na)_2$ (VI), to methyl cuprisalicylate by means of methyl iodide or sulphate in non-aqueous solvents could not be effected, but the latter reagent converts sodium cuprisalicylate in aqueous or aqueous-alcoholic solution into the basic compound (V) in 70% yield. Now sodium cuprisalicylate undergoes hydrolysis in aqueous solution, as is shown by the appearance of a pale green precipitate after a very short time. If the first stage of the hydrolysis is the production of sodium salicylate and a basic compound analogous to (V) (with Na in place of Me), the formation of (V) by means of methyl sulphate can readily be understood and is in agreement with the simple constitutional formula (VI) assigned to sodium cuprisalicylate by Wark (*loc. cit.*).

When concentrated ammonia is added to alcoholic solutions (containing methyl salicylate) of methyl cuprisalicylate and methyl nickelosalicylate, ammine complexes are formed, but only *methyl diamminenickelosalicylate* has been isolated, two ammonia molecules having replaced the two water molecules of the dihydrate (I; X = Ni). This diamminenickel compound crystallises in three forms, two of which are metastable. On heating with water it undergoes rapid hydrolysis, the basic methyl hydroxynickelosalicylate (IV: X = Ni; R = H), identical with that obtained by the hydrolysis of the dihydrate (I), being produced.

Copper and nickel have a co-ordination number of four in the compounds formulated above. Burrows and Wark (*loc. cit.*) regard the aluminium atoms in methyl and ethyl aluminosalicylates and in the salts of the acid $H_2\left[(C_7H_4O_3)_2Al{OH \atop OH_2}\right]$ as having a co-ordination number of six. The latter salts, however, can be simply formulated as $(CO_2M{\cdot}C_6H_4{\cdot}O)_2Al{<}{OH \atop OH_2}$, according to which the aluminium atom has a co-ordination number of four. This is in agreement with the failure of Burrows and Wark to resolve the ion $\left[(C_7H_4O_3)_2Al{OH \atop OH_2}\right]''$ into optical antipodes. The dihydrates and dialcoholates of these salts can then be represented as containing aluminium of co-ordination number six. The properties of methyl aluminosalicylate, $(CO_2Me{\cdot}C_6H_4{\cdot}O)_3Al$, do not lend much support to the contention that it is definitely a stable co-ordinated compound of aluminium, although no doubt there is a tendency towards co-ordination (with the C:O of the carbomethoxy-groups) with chelate ring formation. A comparison of methyl or ethyl aluminosalicylate with ethyl aluminomalonate and of methyl cuprisalicylate with ethyl cupriacetoacetate indicates an increased tendency towards co-ordination with the formation of chelate rings on passing from the salicylate to the open-chain compounds, a tendency which is fully developed in the metallic derivatives of acetylacetone.

EXPERIMENTAL.

Methyl Cuprisalicylate Dihydrate (I; X = Cu).—Copper acetate dihydrate (36 g.; slightly less than the theoretical quantity) in aqueous solution and concentrated ammonia (16 c.c.) were added to a solution of methyl salicylate (50 g.) in about five times its volume of 94% ethyl alcohol. *Methyl cuprisalicylate dihydrate*, which rapidly crystallised, was removed, washed with 50% and finally with 80% alcohol, in which it was practically insoluble, and air-dried (yield, 67%) (Found: C, 47·8; H, 4·5; Cu, 15·8; *M*,

ebullioscopic in acetone, 397. $C_{16}H_{18}O_8Cu$ requires C, 47·8; H, 4·5; Cu, 15·8%; *M*, 401·7).

The dihydrate is a green crystalline solid, soluble in acetone (from which it may readily be recrystallised), methyl salicylate, and benzene, very slightly soluble in ether, and insoluble in chloroform. It begins to decompose at 115°, but suffers partial hydrolysis at lower temperatures owing to interaction with its water of crystallisation.

Hydrolysis. In a vacuum, methyl cuprisalicylate dihydrate lost water and methyl salicylate, very slowly at the ordinary temperature and more rapidly at 100°, but the hydrolysis was incomplete. When the dihydrate was heated in air at 100°, the hydrolysis was also incomplete owing to the escape of some of the water of crystallisation.

A stream of air saturated with water vapour was passed over methyl cuprisalicylate dihydrate heated at 100—105°. After 10 days the weight of the residual *methyl hydroxycuprisalicylate* (IV: X = Cu; R = H) was almost constant (Found: loss, 37·6. Calc. loss due to hydrolysis, 42·3%). The stream of moist air was then replaced by one of dry air; the weight again decreased and became constant after a further 6 days, the *basic compound* (V) having been formed (Found: C, 43·1; H, 3·3; Cu, 28·5. $C_{16}H_{14}O_7Cu_2$ requires C, 43·1; H, 3·2; Cu, 28·6%). The total loss in weight was 44·4% (calc., 44·6%).

Alcoholysis of Methyl Cuprisalicylate Dihydrate.—(i) *With methyl alcohol. Formation of methyl methoxycuprisalicylate* (IV: X = Cu; R = Me). When methyl cuprisalicylate dihydrate was treated with cold methyl alcohol, the green colour changed to blue; very little material dissolved, however, even on boiling. Methyl cuprisalicylate dihydrate was treated with methyl alcohol in a Soxhlet apparatus until the extract was colourless: methyl salicylate and a very little methyl cuprisalicylate dihydrate were identified in the extract. The residue after extraction was *methyl methoxycuprisalicylate* (Found in air-dried material: C, 43·9; H, 4·2; Cu, 25·9; *M*, ebullioscopic in chloroform, 238. $C_9H_{10}O_4Cu$ requires C, 43·9; H, 4·1; Cu, 25·9%; *M*, 245·6).

Methyl methoxycuprisalicylate is a blue solid, non-volatile but decomposed on heating, soluble in chloroform but insoluble in water, methyl alcohol, ether and acetone. It is decomposed by mineral acids. Boiling water completely hydrolyses it to methyl salicylate, methyl alcohol, and copper oxide, but in moist air the methoxy-group only is attacked. When heated at 100° in a stream of wet air (4 days) and thereafter in dry air (4 days), it gave successively methyl hydroxycuprisalicylate (Found: loss, 5·7. Calc.,

5·7%) and the basic compound (V) (Found : total loss, 9·3. Calc. 9·4%. Found in final material : C, 43·1 ; H, 3·3 ; Cu, 28·5. Calc for $C_{16}H_{14}O_7Cu_2$: C, 43·1 ; H, 3·2 ; Cu, 28·6%).

(ii) *With ethyl alcohol.* When methyl cuprisalicylate dihydrate was boiled with ethyl alcohol the bulk of it dissolved to give a deep green solution, but there was a small residue of *cupric ethoxide* probably contaminated with cupric oxide (Found in air-dried material : C, 31·3 ; H, 6·5 ; Cu, 42·6. $C_4H_{10}O_2Cu$ requires C, 31·4 H, 6·6 ; Cu, 41·4%). On further boiling, the green solution turned brown and a small quantity of copper oxide, no doubt formed by hydrolysis by the small amount of water present, separated.

Anhydrous Methyl Cuprisalicylate.—Methyl methoxycuprisalicylate (24·5 g.) was dissolved in a solution in anhydrous acetone of the theoretical quantity of methyl salicylate (15·2 g.). Anhydrous methyl cuprisalicylate separated and was dried over calcium chloride (Found : C, 52·4 ; H, 4·0 ; Cu, 17·4. $C_{16}H_{14}O_3Cu$ requires C, 52·2 ; H, 3·9 ; Cu, 17·4%). It is a green solid which does not crystallise well, is slightly soluble in chloroform and insoluble in acetone, and gives with methyl alcohol the methoxy-derivative (IV : X = Cu ; R = Me).

Methylation of Sodium Cuprisalicylate.—Sodium cuprisalicylate (5 g.), prepared by Wark's method (*loc. cit.*), was dissolved in water (50 c.c.), an excess of methyl sulphate (2 c.c.) immediately added, and the whole shaken at 40° for 15 minutes. The basic compound (V) separated as a dull green solid; it was washed with water and acetone and air-dried (Found : C, 43·0 ; H, 3·2 ; Cu, 28·6%).

Methyl Nickelosalicylate Dihydrate (I ; X = Ni).—An aqueous solution of nickel chloride was added to an alcoholic solution of methyl salicylate (theoretical quantities), the whole being made neutral by the addition of concentrated ammonia solution. The *methyl nickelosalicylate dihydrate* did not crystallise nearly as readily as the copper compound and the yield was much less (Found in air-dried material : C, 48·3 ; H, 4·7 ; Ni, 14·7. $C_{16}H_{18}O_8Ni$ requires C, 48·4 ; H, 4·5 ; Ni, 14·8%).

Methyl nickelosalicylate dihydrate is a light green, crystalline substance, insoluble in water and chloroform but soluble in acetone.

Hydrolysis. When the dihydrate was boiled with water, the colour changed to a darker green and *methyl hydroxynickelosalicylate* (IV : X = Ni ; R = H) was formed (Found in air-dried solid : C, 42·1 ; H, 3·6 ; Ni, 25·9. $C_8H_8O_4Ni$ requires C, 42·3 ; H, 3·5 ; Ni, 25·9%).

Alcoholysis. When the dihydrate was boiled with methyl or ethyl alcohol, a portion dissolved, leaving a green residue of *methyl*

methoxynickelosalicylate (IV : X = Ni ; R = Me) (Found in air-dried material : C, 44·8 ; H, 4·2 ; Ni, 24·2. $C_9H_{10}O_4Ni$ requires C, 44·9 ; H, 4·2 ; Ni, 24·3%) or *methyl ethoxynickelosalicylate* (Found in air-dried material : C, 46·0 ; H, 4·8 ; Ni, 23·0. $C_{10}H_{12}O_4Ni$ requires C, 46·1 ; H, 4·7 ; Ni, 23·0%), respectively. These two substances are insoluble in acetone but soluble in chloroform.

Methyl Diamminenickelosalicylate.—When an excess of concentrated aqueous ammonia was added to a mixture of the theoretical quantities of an aqueous solution of nickel chloride and an alcoholic solution of methyl salicylate, the colour changed from green through blue to deep purple ; purple octahedral crystals of *methyl diamminenickelosalicylate* slowly separated and were washed with aqueous alcohol containing ammonia and dried in an atmosphere containing ammonia (Found : C, 48·6 ; H, 5·2 : N, 7·1 ; Ni, 14·8. $C_{16}H_{20}O_6N_2Ni$ requires C, 48·6 ; H, 5·2 ; N, 7·1 ; Ni, 14·9%). By the addition of a considerable excess of ammonia in this preparation, the diammine compound was obtained in two metastable forms, *viz.*, very fine needles and many-faced crystals of undetermined form, both of which changed fairly rapidly in contact with the solution into the stable octahedral form. Analyses of mixtures of these forms gave figures identical with the above.

Methyl diamminenickelosalicylate is a bright purple, crystalline solid which smells slightly of ammonia and methyl salicylate on exposure to the air, is insoluble in hot or cold acetone, ether and chloroform, and is only slightly attacked by boiling methyl and ethyl alcohols, in which it is insoluble. Heated in a stream of dry air or ammonia, it lost over 40% by weight; only a portion of the ammonia present in the original diammine compound was evolved as such.

Hydrolysis. The diammine compound dissolved in cold water to give a blue (concentrated) or green (dilute) solution which was unstable owing to hydrolysis and immediately started to throw down a green, flocculent precipitate. On boiling, it gave ammonia, methyl salicylate, and a green residue of methyl hydroxynickelosalicylate (Found in the air-dried solid : C, 42·2 ; H, 3·6 ; Ni, 25·8. Calc. for $C_8H_8O_4Ni$: C, 42·3 ; H, 3·5 ; Ni, 25·9%).

Other metallic derivatives of methyl salicylate are under investigation.

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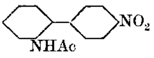
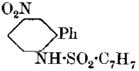
CCCLXVI.—*Investigations in the Diphenyl Series. Part VIII. Derivatives of 2-Amino- and 4-Amino-diphenyl.*

By Frank Bell.

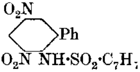
In view of the anomalous nitration of 2-acetamidodiphenyl, which yields 4′-nitro-2-acetamidodiphenyl (I) as a primary product (Scarborough and Waters, J., 1927, 89), the behaviour of 2-p-*toluenesulphonamidodiphenyl* has been examined (compare J., 1926, 2708; 1927, 1129). This compound nitrates with the greatest ease first in the 5-position (II) and then in the 3-position (III). The same ease of substitution is shown by 4′-*nitro*-2-p-*toluenesulphonamidodiphenyl*, since under gentle conditions of nitration



(I.)

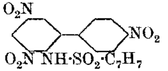


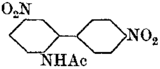
(II.)



(III.)

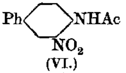
it yields the 3 : 5 : 4′-*trinitro*-derivative (IV). This behaviour is in marked contrast with that of the acetylated bases, for 5 : 4′-dinitro-2-acetamidodiphenyl (V) can be recovered unchanged after solution in fuming nitric acid. 2-Acetamidodiphenyl itself undergoes nitration less readily than 4-acetamidodiphenyl, but the introduction of a nitro-group can be effected without use of sulphuric

(IV.)


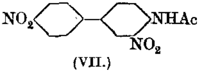


(V.)

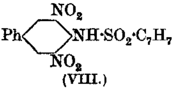
acid, and in this case the primary product is the 5-*nitro*-derivative. Further nitration of this, under all the conditions tried, gave 5 : 4′-dinitro-2-acetamidodiphenyl (V) as the only isolable product. This behaviour accords well with the nitration of 4-acetamidodiphenyl, which gives the 3-nitro-derivative (VI) as primary product and then the 3 : 4′-dinitro-derivative (VII) (Scarborough and Waters, J., 1927, 1134), and these results suggested that 4-*p*-toluenesulphonamidodiphenyl should give the 3 : 5-*dinitro*-derivative (VIII): actually it does nitrate with the utmost ease in the 3 : 5-positions.



(VI.)



(VII.)



(VIII.)

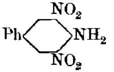
This dinitro-compound (VIII) on hydrolysis readily yields the

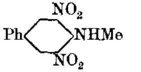
dinitro-base (IX), which is entirely different from the compound to which Fichter and Sulzberger (*Ber.*, 1904, **37**, 878) assigned this constitution. It is more highly coloured and less easily acetylated, and possesses the much greater solubility and lower melting point which compounds with gronps in the 3-position invariably show when compared with compounds having the same substituents in the 4′-position.

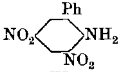
2-p-*Toluenesulphonmethylamidodiphenyl* also nitrates in the 5-*position, but since compounds of this type nitrate so much* less readily and quantitatively than the corresponding unmethylated derivatives, it is preferable to effect nitration before methylation.

A difficulty in acetylating amines having nitro-groups in positions adjacent to the amino-group has been noticed in this work: 3 : 5-*dinitro-4-aminodiphenyl* (IX) and 3 : 5-dinitro-4-methylaminodiphenyl (X) are acetylated only in the presence of sulphuric acid, and the acetyl derivative of 3 : 5-*dinitro-2-aminodiphenyl* (XI) has *not yet been obtained.*

This investigation suggests that the arylsulphonyl group has a

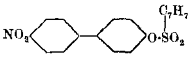

(IX.)

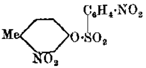

(X.)


(XI.)

considerable advantage over the acetyl group for the preparation of highly nitrated amines in good yield. In higher nitrations (especially in examinations of a quantitative character) the liability of a nitro-group to enter the *p*-toluenesulphonyl residue has to be guarded against. This difficulty can be overcome by the use of the *m*-nitrobenzenesulphonyl derivative or the *p*-nitrobenzenesulphonyl derivative, which has now been made readily accessible (see p. 2776).

The *nitration of the p-toluenesulphonyl derivative* of 4-hydroxydiphenyl to give the 4′-derivative (XII) is in such marked contrast with the nitration of the corresponding derivative of 4-amino-


(XII.)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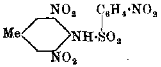
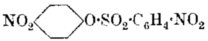
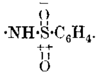

(XIV.)

diphenyl (above) that the first use of *p*-nitrobenzenesulphonyl chloride has been made in contrasting the behaviour of the derivatives of *p*-cresol and of *p*-toluidine : p-*tolyl* p-*nitrobenzenesulphonate* nitrates in the 2-position (XIII), and p-*nitrobenzenesulphon*-p-*tolylamide* in the **3** : 5-positions (XIV), of the toluene nucleus (Me = 1). That the *p*-nitrobenzenesulphonate group is para-

directing is shown by the nitration of *phenyl* p-*nitrobenzenesulphonate* to give the 4-*nitro*-derivative (XV).

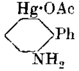
(XV.) 

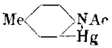
 (XVI.)

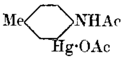
The results outlined above show the powerful orienting nature of the benzenesulphonamido-group, its weakening in the benzenesulphonmethylamido-group, and its complete overthrow in the benzenesulphonates.

It appears that the positively charged sulphur atom of the sulphonamido-group (XVI) facilitates and stabilises the adoption of a negative charge by the nitrogen atom (shown by sodium salt formation), and causes substitution to proceed as in the case of a phenol. The observed sensitiveness of the acetyl group to conditions of nitration can only be explained on the assumption that the acetamido-group enters into salt formation with a strong acid (see, *inter alia*, Dadswell and Kenner, J., 1927, 1102), being thereby converted into a very weakly orienting positive group, so that further substitution naturally resembles that of 2-nitrodiphenyl (Le Fèvre and Turner, J., 1926, 2043; Bell and Kenyon, *ibid.*, p. 2707).

The mercuration of diphenyl derivatives has been little studied, though such mercury compounds would seem to offer a ready source of substances, such as 3-bromo-4-acetamidodiphenyl, otherwise difficult to obtain. A preliminary examination has now been made. 2-Aminodiphenyl monomercurated in the 5-position (XVII), for the product after acetylation and demercuration gave 5-bromo-2-acetamidodiphenyl.


(XVII.)


(XVIII.)


(XIX.)

4-Aminodiphenyl, by analogy with its behaviour on halogenation, must mercurate in the 3-position, but the monomercuri-derivative actually obtained gave 3 : 4′-dibromo-4-acetamidodiphenyl on acetylation and demercuration, a result which is attributed to the fact that, owing to the limited solubility of the mercury compound, the treatment with bromine must take place in hot acetic acid solution.

This observation recalls the ease with which 4-acetamidodiphenyl brominates in the 4′-position (Scarborough and Waters, J., 1926,

557; Kenyon and Robinson, *ibid.*, p. 3050) and in view of the results described earlier in this paper it seemed of interest to examine the bromination of 4-*p*-toluenesulphonamidodiphenyl. Under the experimental conditions used, only the 3-*bromo*-derivative could be isolated, and in poor yield.

3-Bromo-4-hydroxydiphenyl gave a *monomercuri*-derivative, and on treatment with bromine this gave 3 : 5 : 4′-tribromo-4-hydroxydiphenyl: the tribromination of 4-hydroxydiphenyl is not easily accomplished in normal circumstances.

The preparation of the above mercurated acetanilides directed attention to the statement that aceto-*p*-toluidide on mercuration behaves abnormally in giving the anhydro-compound (XVIII) (Schrauth and Schoeller, *Ber.*, 1910, **43**, 2808). The preparation of 3-*acetoxymercuriaceto*-p-*toluidide* (XIX) both by direct mercuration and by acetylation of acetoxymercuri-*p*-toluidine is now described.

2-Aminodiphenyl appears to offer a ready means of obtaining the highly interesting hydrocarbon *o*-diphenylene (Dobbie, Fox, and Gauge, J., 1911, **99**, 683; 1913, **103**, 36) by elimination of its diazotised amino-group with copper powder (a method so successful in the preparation of fluorenone derivatives from aminobenzophenones; Ullmann and Mallet, *Ber.*, 1898, **31**, 1694). However, under the conditions of the present experiments 2-chlorodiphenyl and 2-azodiphenyl were the only isolable products.

EXPERIMENTAL.

2-Aminodiphenyl was prepared in 80% yield by the method of Scarborough and Waters (*loc. cit.*). West's process (J., 1925, **127**, 494) applied to 2-nitrodiphenyl gave a brown 2-aminodiphenyl in only 55% yield.

Attempted Preparation of o-*Diphenylene.*—The filtered diazo-solution prepared from 2-aminodiphenyl (17 g.) was poured into a well-stirred copper paste (from copper sulphate, 125—300 g.). From the reaction mass, by distillation in steam, a small quantity of oily 2-chlorodiphenyl was obtained which crystallised after being shaken with hydrochloric acid and with sodium hydroxide; m. p. 33° (Found: C, 76·6; H, 4·5. Calc.: C, 76·4; H, 4·8%). From the residue after steam distillation, ether extracted a gummy substance; extraction of this with cold petroleum left almost pure 2-azodiphenyl, which crystallised from petroleum in orange needles, or from a very concentrated benzene solution in garnet-red prisms, m. p. 144° (Found: C, 86·4; H, 5·7. Calc.: C, 86·2; H, 5·4%).

5-*Nitro-2-acetamidodiphenyl.*—To a mixture of nitric acid (*d* 1·5; 20 c.c.) and acetic acid (20 c.c.) was added 2-acetamidodiphenyl (10 g.), the temperature being kept below 30°. After ½ hour, the

solution was poured into water and the precipitated solid was removed and boiled with alcohol. The filtered solution deposited 5-*nitro-2-acetamidodiphenyl* in thick orange needles, m. p. 133° (Found : C, 65·3; H, 4·6. $C_{14}H_{12}O_3N_2$ requires C, 65·6; H, 4·7%).

If the temperature is allowed to rise during the nitration, there is formed in addition to the above compound a mixture of more highly nitrated products, which are readily separated owing to their sparing solubility in hot alcohol.

5-*Nitro-2-aminodiphenyl*, obtained by hydrolysis of its acetyl derivative with alcoholic hydrochloric acid, crystallised from alcohol in yellow needles, m. p. 125° (Found : C, 66·8; H, 4·6. $C_{12}H_{10}O_2N_2$ requires C, 67·3; H, 4·7%). The base was readily re-acetylated and converted into its *p*-toluenesulphonyl derivative by the usual methods. 5-*Nitro*-2-p-*toluenesulphonamidodiphenyl* crystallised from acetic acid in thick, pale yellow needles, m. p. 169° (Found : C, 62·2; H, 3·9. $C_{19}H_{16}O_4N_2S$ requires C, 62·0; H, 4·3%).

2-p-*Toluenesulphonamidodiphenyl*, obtained from 2-aminodiphenyl by the usual method, crystallised readily from acetic acid, alcohol, or benzene–petroleum in large rhombs, m. p. 99° (Found : C, 70·6; H, 5·3. $C_{19}H_{17}O_2NS$ requires C, 70·6; H, 5·3%). Methylation yielded 2-p-*toluenesulphonmethylamidodiphenyl*, which crystallised from alcohol in prisms, m. p. 136° (Found : C, 71·2; H, 5·8. $C_{20}H_{19}O_2NS$ requires C, 71·3; H, 5·6%).

Nitration of 2-p-*Toluenesulphonamidodiphenyl*.—(*a*) 2·5 G. were warmed on a water-bath for 7 hours with a mixture of water (25 c.c.) and nitric acid (2·5 c.c.). The product, crystallised from acetic acid, gave pure 5-nitro-2-*p*-toluenesulphonamidodiphenyl (see above).

(*b*) To 3·7 g., dissolved in acetic acid (37 c.c.) at 70°, was added nitric acid (*d* 1·5; 3 c.c.) in acetic acid (3 c.c.), and the whole was maintained at 70° for ¼ hour. On cooling, the liquid filled with prisms of 3 : 5-*dinitro*-2-p-*toluenesulphonamidodiphenyl*, m. p. 186°, unchanged after crystallisation from acetic acid (Found : C, 55·5; H, 3·8. $C_{19}H_{15}O_6N_3S$ requires C, 55·7; H, 3·6%). A solution of this compound (2 g.) in sulphuric acid (4 c.c.) was after ½ hour poured into water and neutralised with ammonia; the precipitated 3 : 5-*dinitro-2-aminodiphenyl* crystallised from alcohol in lustrous yellow plates, m. p. 182° (Found : C, 55·2; H, 3·6. $C_{12}H_9O_4N_3$ requires C, 55·6; H, 3·5%). This base was recovered unchanged after boiling under reflux for 2 hours with acetic anhydride alone, and in the presence of sulphuric acid only oily products were obtained.

Nitration of 2-p-*Toluenesulphonmethylamidodiphenyl*.—(*a*) This

compound (2 g.) was added to a mixture of nitric acid (*d* 1·5; 10 c.c.) and acetic acid (10 c.c.) and after 10 minutes the resultant solution was poured into water. (*b*) 3·5 G. in nitric acid (7 c.c.) were warmed on a water-bath, and the mixture poured into water. The gummy precipitate obtained by either method, when crystallised from acetic acid, furnished pure *5-nitro-2-*p*-toluenesulphonmethylamido-diphenyl* in rosettes of small needles, m. p. 152° (Found: C, 62·4; H, 4·4. $C_{20}H_{18}O_4N_2S$ requires C, 62·8; H, 4·7%). It was proved identical with the substance obtained by the methylation of 5-nitro-2-*p*-toluenesulphonamidodiphenyl (described above).

4′-Nitro-2-acetamidodiphenyl was prepared and hydrolysed by the method of Scarborough and Waters (*loc. cit.*). *4′-Nitro-2-*p*-toluenesulphonamidodiphenyl*, prepared from the base in the usual manner, crystallised from acetic acid in very pale yellow needles, m. p. 163° (Found: C, 62·0; H, 4·4. $C_{19}H_{16}O_4N_2S$ requires C, 62·0; H, 4·4%). This compound (1 g.) in warm acetic acid (10 c.c.) was treated with fuming nitric acid (1 c.c.) in acetic acid (1·5 c.c.). On cooling, the liquid filled with crystals which, recrystallised from acetic acid, gave pure *3:5:4′-trinitro-2-*p*-toluenesulphonamido-diphenyl* in prisms, m. p. 190° (Found: C, 49·8; H, 3·2. $C_{19}H_{14}O_8N_4S$ requires C, 49·8; H, 3·1%). This trinitro-derivative was hydrolysed by dissolving it in concentrated sulphuric acid and after ½ hour pouring the solution on ice. The precipitated *3:5:4′-trinitro-2-aminodiphenyl* crystallised from much alcohol as a bright yellow powder, m. p. 229° (Found: C, 47·7; H, 2·9. $C_{12}H_8O_6N_4$ requires C, 47·3; H, 2·6%).

5:4′-Dinitro-2-acetamidodiphenyl from 5-Nitro-2-acetamidodiphenyl.—To 1 g., dissolved in a mixture of sulphuric acid (3 c.c.) and acetic acid (1·5 c.c.), fuming nitric acid (0·8 c.c.) in acetic acid (1 c.c.) was added. After 12 hours, the solution was poured into water; the precipitate obtained, after being washed with alcohol, crystallised from alcohol–pyridine in prismatic needles, m. p. 208°, identical with the product obtained by the nitration of 4′-nitro-2-acetamido-diphenyl. 5:4′-Dinitro-2-aminodiphenyl did not react with *p*-toluenesulphonyl chloride under the ordinary conditions.

*Nitration of 4-*p*-Toluenesulphonamidodiphenyl.*—To 10 g., dissolved in acetic acid (10 c.c.) at 80°, fuming nitric acid (10 c.c.) in acetic acid (10 c.c.) was added. On cooling, pure *3:5-dinitro-4-*p*-toluenesulphonamidodiphenyl* (9·5 g.) separated; it crystallised from acetic acid in long needles, m. p. 189° (Found: C, 55·4; H, 3·7. $C_{19}H_{15}O_6N_3S$ requires C, 55·7; H, 3·6%). Hydrolysis in the usual manner gave *3:5-dinitro-4-aminodiphenyl*, which crystallised from benzene in orange-red needles, m. p. 177° (Found: C, 55·6; H, 3·5. $C_{12}H_9O_4N_3$ requires C, 55·6; H, 3·5%). This base was not attacked

by acetic anhydride alone, but in the presence of sulphuric acid it gave 3 : 5-*dinitro-4-acetamidodiphenyl*, which crystallised from alcohol in pale yellow needles, m. p. 146° (Found : C, 55·8; H, 3·8. $C_{14}H_{11}O_5N_3$ requires C, 55·8; H, 3·6%).

3 : 5-*Dinitro*-4-p-*toluenesulphonmethylamidodiphenyl*, obtained from the corresponding base by methylation, crystallised from acetic acid in needles, m. p. 144° (Found : C, 55·9; H, 4·3. $C_{20}H_{17}O_6N_3S$ requires C, 56·2; H, 4·0%). Hydrolysis with sulphuric acid gave the already described 3 : 5-dinitro-4-methylaminodiphenyl (Bell and Kenyon, J., 1926, 2710), which with acetic anhydride, in the presence of sulphuric acid, gave 3 : 5-*dinitro-4-acetomethylamidodiphenyl*. This substance crystallised from alcohol in lustrous yellow needles, m. p. 149° (Found : C, 57·2; H, 4·0. $C_{15}H_{13}O_5N_3$ requires C, 57·2; H, 4·1%).

3 : 4′-*Dinitro-4-acetamidodiphenyl*.—4-Acetamidodiphenyl (5 g.) was added to ice-cold fuming nitric acid (15 c.c.) and after ½ hour the solution was poured on ice. The precipitate, after being washed with alcohol, crystallised from pyridine in pale yellow needles, m. p. 240°. 2 G., when heated under reflux with alcoholic hydrochloric acid (100 c.c.), rapidly dissolved to a clear solution which soon deposited orange needles of 3 : 4′-dinitro-4-aminodiphenyl, readily recrystallised from pyridine. This base did not react with *p*-toluenesulphonyl chloride under the usual conditions.

p-*Nitrobenzenesulphonyl Chloride*.—To a boiling solution of *p*-chloronitrobenzene (250 g.) in alcohol (600 c.c.) was added in portions the product obtained by fusing crystalline sodium sulphide (200 g.) and sulphur (35 g.). The mixture was heated for ½ hour and then cooled to about 50°. The solid product, after being washed with alcohol, water, and again with alcohol, was boiled with acetic acid (500 c.c.), cooled, collected, dried, and divided into 40 g. batches. Each batch was added to fuming nitric acid (10 c.c.), and the solution was warmed for 1 hour, diluted with water (500 c.c.), and filtered. The combined filtrates were evaporated almost to dryness and again after the addition of more water. The residue was neutralised with dilute aqueous ammonia, and ammonium *p*-nitrobenzenesulphonate obtained in large crystals. This ammonium salt (100 g.) was heated with chlorosulphonic acid (100 c.c.) at 100° for 1 hour, and the cooled solution poured on ice. The precipitate was collected rapidly, dried, and crystallised from benzene–light petroleum, from which *p*-nitrobenzenesulphonyl chloride separated in large prisms, m. p. 80° (yield, 70 g.).

The derivatives of this chloride crystallise with remarkable ease. By interaction with alcoholic sodium ethoxide in ethereal solution it gives *ethyl* p-*nitrobenzenesulphonate*, large plates, m. p. 91° (Found :

C, 42·1; H, 3·7. $C_8H_9O_5NS$ requires C, 41·6; H, 3·9%), and with menthol in pyridine *menthyl* p-*nitrobenzenesulphonate*, long needles, m. p. 72° (Found: C, 55·8; H, 6·7. $C_{16}H_{23}O_5NS$ requires C, 56·3; H, 6·7%). The following sulphonates and sulphonamides were obtained by interaction of the components in pyridine solution and crystallisation of the product from acetic acid.

Phenyl p-*nitrobenzenesulphonate*, needles, m. p. 114° (Found: C, 51·8; H, 3·4. $C_{12}H_9O_5NS$ requires C, 51·6; H, 3·2%). *m-Nitrophenyl* p-*nitrobenzenesulphonate*, m. p. 133° (Found: C, 44·9; H, 2·5. $C_{12}H_8O_7N_2S$ requires C, 44·5; H, 2·5%). p-*Nitrophenyl* p-*nitrobenzenesulphonate*, m. p. 156° (Found: C, 45·0; H, 2·5%).

Nitration of Phenyl p-*Nitrobenzenesulphonate*.—2·5 G. were added slowly to ice-cold fuming nitric acid (5 c.c.), and the resulting solution poured on ice. The precipitate (2·9 g., m. p. 140—150°), when crystallised from acetic acid, furnished *p*-nitrophenyl *p*-nitrobenzenesulphonate (2·4 g.).

p-*Tolyl* p-*nitrobenzenesulphonate*, m. p. 106° (Found: C, 53·7; H, 3·7. $C_{13}H_{11}O_5NS$ requires C, 53·2; H, 3·8%).

3-*Nitro*-p-*tolyl* p-*nitrobenzenesulphonate*, m. p. 136° (Found: C, 46·4; H, 2·9. $C_{13}H_{10}O_7N_2S$ requires C, 46·1; H, 3·0%).

2-*Nitro*-p-*tolyl* p-*nitrobenzenesulphonate*, m. p. 116° (Found: C, 45·9; H, 3·0%).

Nitration of p-*Tolyl* p-*Nitrobenzenesulphonate*.—4·5 G. were added to fuming nitric acid (10 c.c.) and the solution was poured on ice. The resulting precipitate (m. p. 100—110°; 3·6 g.) on crystallisation from acetic acid furnished 2-nitro-*p*-tolyl *p*-nitrobenzenesulphonate (2·5 g.).

p-*Nitrobenzenesulphon*-p-*tolylamide* has m. p. 179—180° (Found: C, 54·0; H, 3·7. $C_{13}H_{12}O_4N_2S$ requires C, 53·5; H, 4·1%). This compound (2·5 g.) and nitric acid (5 c.c.) were warmed on a steam-bath until a vigorous reaction took place. The mixture was diluted with water and the precipitate obtained, on crystallisation from acetic acid, gave p-*nitrobenzenesulphon*-3 : 5-*dinitro*-p-*tolylamide* (XIV), m. p. 185° (Found: C, 40·8; H, 3·0. $C_{13}H_{10}O_8N_4S$ requires C, 40·8; H, 2·6%), which was identified by hydrolysis to 3 : 5-dinitro-*p*-toluidine (acetyl derivative, m. p. 194°).

5-*Acetoxymercuri-2-acetamidodiphenyl*.—To a solution of 2-aminodiphenyl (5 g.) in alcohol (40 c.c.) was added mercuric acetate in water (40 c.c. containing acetic acid, 2 c.c.). The precipitated oil, after being dried, was warmed with acetic anhydride; the *product crystallised from aqueous acetic acid in needles, m. p. 200°* (Found: Hg, 43·2. $C_{16}H_{15}O_3NHg$ requires Hg, 42·7%). Treated with bromine in acetic acid, this compound gave 5-bromo-2-acetamidodiphenyl, crystallising from aqueous alcohol in long needles,

m. p. 128°, identical with the compound prepared by the method of Scarborough and Waters (*loc. cit.*).

Mercuration of 4-Aminodiphenyl.—Mercurated by the method described above, 4-aminodiphenyl gave a white precipitate, m. p. 167° (Found: Hg, 54·7%), which crystallised from aqueous acetic acid without change (Found: Hg, 54·8%). It appears to be the substance $C_6H_5{\cdot}C_6H_3{<}\overset{NH}{\underset{Hg}{|}}$, which requires Hg, 54·6%. Its solution in warm acetic acid, on cooling, deposited needles of 3-*acetoxymercuri*-4-*acetamidodiphenyl*, m. p. 205° (Found: Hg, 42·9. $C_{16}H_{15}O_3NHg$ requires Hg, 42·7%). On repeated crystallisation from boiling acetic acid this compound lost its crystalline character and increased in melting point and mercury content (44·1, 46·5%). The product, m. p. 205°, on treatment with bromine (1 mol.) in acetic acid gave gummy material, but with an excess of bromine it gave a compound, sparingly soluble in alcohol and crystallising from benzene in colourless needles, m. p. 196°. This must be 3 : 4′-dibromo-4-acetamidodiphenyl (Scarborough and Waters, J., 1926, 561), and the presence of this additional bromine atom accords well with the propensity of 4-acetamidodiphenyl to brominate in the 4′-position.

Bromination of 4-p-*Toluenesulphonamidodiphenyl.*—To 6 g. in warm acetic acid (50 c.c.) was added bromine (3 g.) in acetic acid (15 c.c.). After cooling, the solution was filtered from a small amount of unchanged material and poured into water. The gummy precipitate, after repeated crystallisation from alcohol, gave 3-*bromo*-4-p-*toluenesulphonamidodiphenyl* in large prisms, m. p. 119° (Found: C, 56·4; H, 4·2. $C_{19}H_{16}O_2NBrS$ requires C, 56·7; H, 4·0%). It was identical with the compound obtained by the interaction of *p*-toluenesulphonyl chloride and 3-bromo-4-aminodiphenyl in pyridine solution.

3-Bromo-4-hydroxydiphenyl furnished a uniform *monomercuri*-derivative, which crystallised from acetic acid in needles, m. p. 235° (Found: Hg, 39·7, 39·4. $C_{14}H_{11}O_3BrHg$ requires Hg, 39·5%), but 4-hydroxydiphenyl gave a mixture of more highly mercurated derivatives (Found: Hg, 61·7, 60·6. $C_{16}H_{14}O_5Hg_2$ requires Hg, 58·4%). When treated with bromine in acetic acid, these compounds all gave 3 : 5 : 4′-tribromo-4-hydroxydiphenyl.

3-*Acetoxymercuriaceto*-p-*toluidide.*—Mercuric acetate (20 g.) was added to aceto-*p*-toluidide (10 g.) in acetic acid (100 c.c.) and the solution, after boiling under reflux for 1 hour, was filtered from precipitated mercurous acetate and evaporated under diminished pressure. The residue was boiled with water and crystallised successively from aqueous alcohol, acetic anhydride, and acetic acid,

3-*acetoxymercuriaceto*-p-*toluidide* being obtained in long needles, m. p. 178° (Found: Hg, 49·3, 49·6. $C_{11}H_{13}O_3NHg$ requires Hg, 49·3%). It was more easily prepared by dissolving 3-acetoxymercuri-*p*-toluidine (m. p. 189° decomp.: obtained in quantitative yield from *p*-toluidine) in acetic anhydride, and recrystallising the product until of constant melting point. Treated with bromine in acetic acid, it gave 3-bromoaceto-*p*-toluidide contaminated by dibromoacetotoluidide.

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CCCLXVII.—*The Interaction of Bromine with Acetic Anhydride. Part IV. Bromination and Chlorination compared.*

By HERBERT BEN WATSON and EMRYS HADDON ROBERTS.

INVESTIGATION of the reactions of chlorine with acetic anhydride, acetyl chloride, and acetic acid has yielded results which indicate that chlorination is in many respects similar to bromination, but nevertheless presents some striking contrasts.

It was shown by Gal (*Ann. Chim. Phys.*, 1862, **66**, 187) that the chlorination of acetic anhydride yields acetyl chloride and monochloroacetic acid, products which are the analogues of those obtained by the action of bromine. The authors now find that the velocity curves resemble in form those obtained by Orton, Watson, and Hughes in bromination experiments (Part II, J., 1927, 2458), and that the reaction is similarly accelerated by acid chlorides, ferric chloride, sulphuric acid, and iodine or iodine chloride. That changes of an identical character take place in the two cases is proved conclusively by the constancy of the values of C obtained by use of the expression $C = 1/t \cdot \log_e (a + P)/(a + P - x)$, which was deduced by Orton, Watson, and Hughes for bromination. It is clear, therefore, that chlorination, like bromination, proceeds by two routes, involving in the one the halogenation of the acid chloride and in the other the preliminary enolisation of the anhydride.

Chlorine, however, reacts far more slowly than bromine. The values of the constants in Tables II and III leave no doubt that this difference is due entirely to a difference in the speeds of halogenation of the acyl halides, whilst the velocity of enolisation of the anhydride is unaffected.

Quinoline, pyridine, and sodium acetate, which inhibit the bromination of acetic anhydride (Part II), have no similar effect on chlorination; the first-named two, indeed, accelerate somewhat the disappearance of chlorine. The influence of these substances on bromination has been attributed by one of us (Watson, Part III, J., 1927, 3065) to their reaction with a trace of hydrogen bromide produced in the bromination of the enolised anhydride, for by removal of the halogen acid the series of reactions involving the acid bromide will be eliminated, and in addition the speed of enolisation of the anhydride very considerably decreased. The catalytic effect of the base upon the enolisation appears to be but small in comparison with that of halogen acid.

The remarkable difference between bromination and chlorination may find an explanation in the following considerations. Acetic anhydride, in spite of its fairly high dielectric constant, behaves in all respects as a " normal " liquid (compare Jones and Betts, this vol., p. 1178; Jones, *ibid.*, p. 1195). In a medium of this type, the halogen acids are doubtless covalent compounds (compare Sidgwick, " The Electronic Theory of Valency," p. 93), and reaction with the base would consist in the giving up of a proton covalently linked to the halogen. In presence of an excess of bromine, hydrogen bromide exists almost entirely in combination as the perbromide HBr_3: the powerful electron-affinity of the two co-ordinated bromine atoms (Ingold, *Ann. Report*, 1926, 140) will bring about a loosening of the proton, thus enabling its appropriation by the base to take place readily:

$$\begin{matrix}-C\\-C\end{matrix}\!>\!N\!: + H\!:\!\ddot{\underset{\cdot\cdot}{Br}}\!:\!(Br_2) \longrightarrow \begin{matrix}-C\\-C\end{matrix}\!>\!N\!:\!H^{+} + :\!\ddot{\underset{\cdot\cdot}{Br}}\!:\!(Br_2)^{-}.$$

An analogy, consisting in the withdrawal of a proton covalently attached to *oxygen*, is found in the production of hydroxo-ammines of cobalt and chromium by the action of pyridine or ammonia on the corresponding aquo-ammines, as exemplified in the reaction $[Cr(NH_3)_2(H_2O)_4]Cl_3 + 2C_5H_5N = [Cr(NH_3)_2(H_2O)_2(OH)_2]Cl + 2C_5H_5N,HCl$ (Werner, *Ber.*, 1907, **40**, 272, 4098, 4113, 4133; Pfeiffer, *ibid.*, p. 3129).

In the case of hydrogen chloride there is but little perhalide formation (compare the relative effects of hydrogen bromide and chloride on the bromination and chlorination, respectively, of acetanilide : Orton and Jones, *Brit. Assoc. Rep.*, 1910, 99); weakening of the covalent bond does not therefore occur, and the base has no opportunity of combining with the proton. The hydrogen chloride is thus free to react with a molar quantity of acetic anhydride : $HCl + (CH_3{\cdot}CO)_2O \rightleftharpoons CH_3{\cdot}COCl + CH_3{\cdot}CO_2H$; the chlorin-

ation of the acid chloride then proceeds, and, moreover, the enolisation of the anhydride is catalysed not only by the small quantity of halogen acid present in the above equilibrium but also by the base. Chlorination is therefore not inhibited but accelerated, and the larger the quantity of base introduced the greater is the acceleration.

Acetyl nitrate has been shown to inhibit very powerfully the bromination of acetic anhydride, by oxidation of halogen acid (Parts II and III). As would be expected from the relative indifference of hydrogen chloride to oxidising agents, it does not inhibit chlorination. Addition of a little nitric acid, in fact, accelerates the reaction, an effect which indicates incomplete conversion of the acid into acetyl nitrate.

Chlorination of Acetyl Chloride.—The relatively slow speed of chlorination of acetyl chloride, which is indicated by the experiments described in the foregoing, has been confirmed by an examination of the reaction of chlorine at 25° with the acid chloride itself. Acetyl chloride, in fact, reacts with chlorine more slowly than with bromine (see Table IV). Contrary to expectation, the rate of disappearance of chlorine has been found to *increase* as the reaction proceeds. This peculiarity is not the result of a comparatively rapid substitution of a second hydrogen atom, since chloroacetyl chloride does not react with chlorine appreciably at 25°, but it is due rather to side reactions, which consist, partly at least, in the replacement of the carbonyl oxygen by two atoms of chlorine, followed by further chlorination of the $C_2H_3Cl_3$ to give hexachloroethane, the odour of which is unmistakable in the product (compare the action of phosphorus pentachloride on acetyl chloride: Hübner, *Annalen*, 1861, **120**, 330; Hübner and Müller, *Z. Chem.*, 1870, 328).

Addition of a small quantity of iodine catalyses the production of chloroacetyl chloride so powerfully (compare Jazukowitsch, *Z. Chem.*, 1868, 234) that the side reactions are now imperceptible, and the velocity is proportional to the concentration of chlorine. The side reactions are masked in the same manner when acetyl chloride reacts with chlorine in acetic anhydride medium (preceding section).

Chlorination of Acetic Acid.—A study of the reaction of chlorine with acetic acid at 100° has yielded results resembling those previously obtained by one of us for bromination (Watson, J., 1925, **127**, 2067); the reaction, however, is slower. A powerful acceleration results from the introduction of a small quantity of acetyl chloride, to which the catalytic influence of acetic anhydride (Hentschel, *Ber.*, 1884, **17**, 1286) and also that of phosphorus

and phosphorus pentachloride (Brückner, *Z. angew. Chem.*, 1927, **40**, 973) are doubtless to be ascribed (compare the interpretation of the effects of acetic anhydride and phosphorus on bromination : Watson, *loc. cit.*). The velocity is proportional to the quantity of acetyl chloride added, and different acid chlorides have identical effects.

These facts lead to the conclusion that chlorination proceeds through a series of reactions analogous to those suggested for bromination (Watson, *loc. cit.*), *viz.*,

$$CH_3{\cdot}COCl + Cl_2 = CH_2Cl{\cdot}COCl + HCl,$$
$$CH_2Cl{\cdot}COCl + CH_3{\cdot}CO_2H = CH_3{\cdot}COCl + CH_2Cl{\cdot}CO_2H,$$

preceded, when the chloride of another acid is added initially, by

$$R{\cdot}COCl + CH_3{\cdot}CO_2H = CH_3{\cdot}COCl + R{\cdot}CO_2H.$$

In presence of an acid bromide, the velocity of *bromination* of acetic acid has been shown to vary directly as the concentration of the halogen, and this is in harmony with the mechanism suggested. A similar relationship is not found in the analogous case of chlorination in presence of an acid chloride, for the velocity of the reaction decreases less rapidly than does the concentration of chlorine. This observation is accounted for, however, by the existence of the side reactions referred to in the preceding section

Hydrogen chloride accelerates the chlorination of acetic acid and its influence is probably due to the production of a trace of acid chloride (compare the effect of hydrogen bromide on bromination : Watson, *loc. cit.*). The powerful enolising agents sulphuric acid and ferric chloride, on the other hand, have very little effect, a fact which indicates that reaction of the halogen with the enolic form of acetic acid occurs only to a very small extent. The part played by the enolide, though insignificant, may perhaps contribute to some extent to the absence (noted above) of a simple relation between the fall in concentration of chlorine and the velocity In bromination, its effect is masked by the relatively great speed of the reaction of bromine with acetyl bromide, or is perhaps to some extent balanced by perbromide formation.

Inactivity of Iodine.—Iodine does not attack acetic anhydride at 25°, nor does introduction of hydrogen iodide or of sulphuric acid lead to reaction. On heating the anhydride with iodine at 100° for several hours there is little fall in iodine concentration but some carbonisation (compare Gal, *loc. cit.*). No reaction takes place when acetic acid is heated witb iodine at 100°.

EXPERIMENTAL.

The acetic anhydride was obtained by fractional distillation of "reagent" material. The acid chlorides and other substances

mployed were purified as described in the earlier papers of this eries. Each reaction mixture (25 c.c.) contained 5 c.c. of a solution f chlorine in carbon tetrachloride; in preparing this solution, hlorine from a cylinder was passed through water, permanganate, nd sulphuric acid and then into the solvent. The velocity measurenents were carried out at 25° in well-stoppered flasks as described reviously, 2 c.c. being withdrawn for each titration. The anhydride ras used throughout in large excess. Titres are stated in c.c. of V/10-thiosulphate.

TABLE I.

Substance added.	Conc., *M*.	Initial titre.	Fall in titre after (hours) 50.	100.	150.	200.	250.	300.	350.
il …………		9·85	0·55	1·60	2·80	3·95	5·00	5·95	6·85*
il …………		4·90	0·25	0·55	1·00	1·40	1·95	2·55	3·10†
H_3·COCl …	0·112	11·15	1·20	2·30	3·40	4·60			
H_3·COCl …	0·225	11·30	2·15	3·90	5·60				
$_6H_5$·COCl …	0·225	12·05	1·80	3·75	5·60				
$_5H_5N$ ……	0·010	9·10	1·80	3·20	4·30	5·10	5·60		
$_9H_7N$ ……	0·008	12·80	2·50	4·70	6·75	8·05	8·95		
INO_3 ………	0·015	8·20	1·50	3·05	3·95	4·65	5·05	5·20	
H_3·CO_2Na…	0·005	11·35	0·80	1·80	2·75	3·70	4·60	5·45	6·35‡

The fall in titre after 450 hours was 8·05*, 3·85†, and 7·75‡.

Substance added.	Conc., *M*.	Initial titre.	Fall in titre after (mins.) 15.	30.	45.	60.	90.	120.	240.
$_5H_5N$ ……	0·118	11·50	3·90	5·75	6·65	7·25	8·00	8·30	8·85
$_9H_7N$ ……	0·100	11 00	1·35	2·25	2·80	3·15	3·65	4·00	4·90
I_2SO_4 ………	0·001	11·05	0·40	0·80	1·25	1·75	2·60	3·55	7·05
I_2SO_4 ………	0·002	11·05	0·60	1·35	2·15	2·85	4·25	5·65	10·55
odine ………	0·003	9·85	0·35	0·80	1·60	2·50	4·65	8·25	
odine ………	0·006	9·75	0·60	1·60	3·40	5·20	9·10		

Substance added.	Conc., *M*.	Initial titre.	Fall in titre after (mins.) 5.	10.	15.	20.
Cl ………………	0·003	10·55	2·00	5·05	7·05	9·00
Cl ………………	0·006	9·20	3·30	5·70	7·05	
eCl_3 ……………	0·003	9·85	0·40	1·90	3·50	5·50
eCl_3 ……………	0·007	9·90	2·05	6·35	Gone	

he reaction of bromine with acetic anhydride at 25°, when carried ut under the same conditions as the above (5 c.c. of carbon tetrahloride in 25 c.c. of reaction mixture), gave the following:

Initial titre.	Fall in titre after (hours) 1.	2.	3.	4.	5.
11·60	0·75	3·10	6·05	8·40	10·50

omparison with the figures recorded in Part II for the bromintion of pure acetic anhydride shows *the very marked retardation* roduced by the carbon tetrachloride (compare Watson, this vol., . 1138).

Reaction of Halogens with Acetic Anhydride and Excess of Acyl Halide.—As in the above experiments, 25 c.c. of reaction mixture contained 5 c.c. of a solution of the halogen in carbon tetrachloride. Titres are stated in c.c. of $N/50$-thiosulphate, and time in minutes. The constants are calculated from the formula $C = 1/t \,.\, \log_e (a + P)/(a + P - x)$ (Part II), where $C = k$[acyl halide] and $C' = k'[Ac_2O]$, k and k' being the velocity coefficients for the halogenation of the acyl halide and the enolisation of the anhydride, respectively, and $P = C'/C$.

TABLE II.

Chlorine and Excess of Acetic Anhydride and Acetyl Chloride.

$[Ac_2O] = 6{\cdot}376M$, $[AcCl] = 2{\cdot}915M$, $P = 1{\cdot}10$.

$a = 0{\cdot}1215M$.			$a = 0{\cdot}0344M$.		
Time.	Titre.	C.	Time.	Titre.	C.
0	24·30		0	6·88	
120	21·10	0·000106	60	5·48	0·000097
200	*19·40*	*0·000104*	*125*	*3·92*	*0·000102*
395	14·50	0·000104	152	3·20	0·000106
600	9·50	0·000104	185	2·45	0·000106
660	8·10	0·000104	240	1·18	0·000106
	Mean	0·000104		Mean	0·000104

$k = 0{\cdot}0000357$, $C' = 0{\cdot}0001144$, $k' = 0{\cdot}0000179$.

TABLE III.

Bromine and Excess of Acetic Anhydride and Acetyl Bromide.

(These experiments differ from those of Orton, Watson, and Hughes in Part II, in that 5 c.c. of carbon tetrachloride were present in each 25 c.c. of reaction mixture.)

$[Ac_2O] = 6{\cdot}245M$, $[AcBr] = 2{\cdot}932M$, $P = 0{\cdot}0029$.

$a = 0{\cdot}1138M$.			$a = 0{\cdot}0454M$.		
Time.	Titre.	C.	Time.	Titre.	C.
0	22·75		0	9·08	
20	10·25	0·0384	10	6·08	0·0373
32	6·28	0·0382	15	4·78	0·0391
40	*4·05*	*0·0403*	*20*	3·82	0·0391
	Mean	0·0390		Mean	0·0385

$k = 0{\cdot}0132$, $C' = 0{\cdot}0001125$, $k' = 0{\cdot}0000180$.

The values of k' are in excellent agreement in the two sets of experiments.

Chlorination of Acetyl Chloride.—The distillation of the acid chloride and the velocity measurements (for which 5 c.c. of the solution of chlorine in carbon tetrachloride were added to 25 c.c. of acetyl chloride) were carried out in the apparatus described by one of us (Watson, this vol., p. 1139). The acetyl chloride was

throughout in large excess. The velocity of bromination under identical conditions is given for comparison. Titres are expressed in c.c. of *N*/10-thiosulphate.

TABLE IV.

25 c.c. AcCl + 5 c.c. soln. of Cl in CCl_4.		25 c.c. AcCl + 5 c.c. soln. of Br in CCl_4.		25 c.c. AcCl + 5 c.c. soln. of Cl in CCl_4 + 0·03*M*-iodine.		
Time (hrs.).	Titre.	Time (hrs.).	Titre.	Time (mins.).	Titre.	k_1.
0	12·25	0	12·00	0	7·95	
12	10·10	6	9·85	30	5·65	0·0114
24	7·55	12	7·85	60	4·05	0·0112
36	4·60	18	5·85	90	2·85	0·0114
48	1·45	24	4·40			
		30	2·70			

Chlorination of Acetic Acid.—The acetic acid was purified by the method of Orton and Bradfield (J., 1927, 983). It melted at 16·45°, was stable to halogens at the ordinary temperature, and gave results identical with those obtained by use of the best Kahlbaum acid. A solution of chlorine in this acid was used in making up the reaction mixtures, which were heated in sealed tubes at 100° in portions of 2 c.c. The acetic acid was throughout in large excess. Titres are stated in c.c. of *N*/10-thiosulphate.

TABLE V.

	Titre of 2 c.c.			
Time (hrs.).	Pure $CH_3\cdot CO_2H$.	Pure $CH_3\cdot CO_2H$.	$CH_3\cdot CO_2H$ + 0·19*M*-H_2SO_4.	$CH_3\cdot CO_2H$ + 0·045*M*-$FeCl_3$.
0	17·95	9·68	9·38	8·02
2	15·42	7·70	6·90	5·82
4	14·08	5·88	4·25	3·52
6	12·12	3·68	2·00	1·85
8	8·62	1·72	0·70	0·50
10	4·20	0·38		

	Titre of 2 c.c.	
Time (mins.).	$CH_3\cdot CO_2H$ + 0·24*M*-HCl.	$CH_3\cdot CO_2H$ + 0·56*M*-HCl.
0	8·82	8·80
45	7·05	6·42
90	5·65	4·42
180	3·00	1·65
240	1·48	0·60

Substance added.	Conc., *M* (=*C*).	Titre after (mins.) 0.	5.	10.	15.	20.	30.	First value of k_1.	k_1/C.
$CH_3\cdot COCl$ ...	0·093	8·98	7·05	4·98	3·20	1·42		0·048	0·51
$CH_2Cl\cdot COCl$	0·070	8·40	7·00	5·82	4·58	3·20		0·035	0·50
$C_6H_5\cdot COCl$ ...	0·079	8·32	6·90	5·50	3·92	2·48		0·037	0·47
$CH_3\cdot COCl$ ...	0·052	8·80		6·75		5·22	2·92*	0·026	0·50
$CH_2Cl\cdot COCl$	0·054	10·15		7·70		5·45	2·95†	0·027	0·51
$C_6H_5\cdot COCl$ ...	0·052	10·52		8·22		5·82	3·21‡	0·025	0·48

The titre after 40 mins. was 1·00*, 1·15†, and 2·10‡.

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CCCLXVIII.—*Conversion of Hydroaromatic into Aromatic Compounds. Part III. 3 : 5-Dichloro-1-phenyl-*$\Delta^{2:4}$-cyclo*hexadiene and its Behaviour with Chlorine.*

By LEONARD ERIC HINKEL and DONALD HOLROYDE HEY.

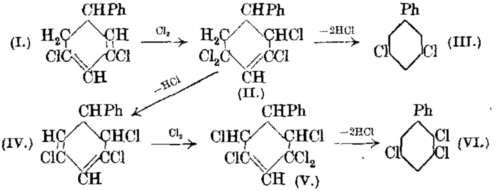
IN previous papers (*J.*, 1924, **125**, 1847; this vol., p. 1200) it has been shown that halogenated derivatives of phenyldihydroresorcinol are converted into aromatic compounds much more readily than the corresponding derivatives of dimethyldihydroresorcinol. For instance, 4 : 5 : 5-tribromo-1-phenyl*cyclo*hexan-3-one readily yields an aromatic compound directly, whereas 4 : 5 : 5-trichloro-1 : 1-dimethyl*cyclo*hexan-3-one only does so through the stable intermediate 4 : 5-dichloro-1 : 1-dimethyl-Δ^5-*cyclo*hexen-3-one; and 4 : 5 : 5 : 6-tetrabromo-1-phenyl*cyclo*hexan-3-one yields 4 : 5-dibromo-3-hydroxydiphenyl directly, whereas 4 : 5 : 5 : 6-tetrachloro-1 : 1-dimethyl*cyclo*hexan-3-one readily changes into the stable intermediate 4 : 5 : 6-trichloro-1 : 1-dimethyl-Δ^5-*cyclo*hexen-3-one. Moreover, cleavage of the ring by hydrolysis cannot be achieved in dimethyldihydroresorcinol, but can be readily effected in the case of phenyldihydroresorcinol (Vorländer, *Annalen*, 1897, **294**, 317; *Ber.*, 1894, **27**, 2057; compare also Crossley, J., 1901, **79**, 138).

The greater readiness with which the derivatives of phenyldihydroresorcinol are converted into aromatic compounds is only to be expected, since in the one case the transformation necessitates the migration of a methyl group, whereas in the other the more mobile hydrogen atom is involved, and this is further borne out in the present investigation on 3 : 5-*dichloro*-1-*phenyl*-$\Delta^{2:4}$-cyclo*hexadiene* (I).

Knoevenagel (*Ber.*, 1894, **27**, 2337) isolated a liquid impure dichlorophenyl*cyclo*hexadiene by the action of phosphorus pentachloride (2 mols.) on phenyldihydroresorcinol, but the structure he assigned to it is no longer tenable (compare Crossley and Le Sueur, J., 1902, **81**, 821). Since both di- and tri-methyldihydroresorcinols on treatment with phosphorus pentachloride give, in addition to a dichloro*cyclo*hexadiene, 3 : 5-dichloro-*o*-xylene and 3 : 5-dichloro-1 : 2 : 6-trimethylbenzene, respectively (Crossley and Le Sueur, J.,

1902, **81**, 1533; Crossley and Hills, J., 1906, **89**, 875), 3 : 5-dichlorodiphenyl (III) should in like manner be formed during the action of phosphorus pentachloride on phenyldihydroresorcinol. This has now been shown to be the case. The main product of the action, however, is 3 : 5-dichloro-1-phenyl-$\Delta^{2:4}$-*cyclo*hexadiene (I). This compound readily absorbs chlorine, and the *tetrachloro*-compound (II) produced rapidly loses hydrogen chloride (2 mols.) on warming, giving an 80% yield of 3 : 5-dichlorodiphenyl (III). The constitution of (III) has been established by its synthesis as carried out by Scarborough and Waters (J., 1927, 89), who describe it as an oil. The compound has now been obtained by both methods as a crystalline solid.

When an excess of chlorine is passed into a hot solution of 3 : 5-dichloro-1-phenyl-$\Delta^{2:4}$-*cyclo*hexadiene in chloroform, in addition to 3 : 5-dichlorodiphenyl, a small quantity of 2 : 3 : 5-*trichlorodiphenyl* (VI) is produced, the constitution of which has been confirmed by its synthesis from 3 : 5-dichloro-2-aminodiphenyl. Its formation is explained in the following manner. Loss of one molecule of hydrogen chloride from the tetrachloro-compound (II) gives the trichloro-compound (IV). This may partly lose hydrogen chloride to give 3 : 5-dichlorodiphenyl or may further combine with chlorine, giving an unstable pentachloro-compound (V), which readily loses hydrogen chloride to give 2 : 3 : 5-trichlorodiphenyl (VI) (compare Crossley, J., 1904, **85**, 264; Hinkel, J., 1920, **117**, 1296).

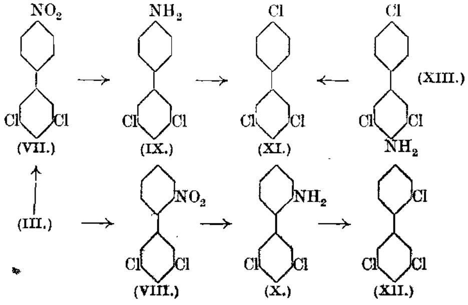


In marked contrast with the action of chlorine on 3 : 5-dichloro-1 : 1-dimethyl-$\Delta^{2:4}$-*cyclo*hexadiene (Hinkel, *loc. cit.*), which gives rise to a pentachlorodimethyl*cyclo*hexene in addition to the two trichloro-*o*-xylenes and tetrachloro-*o*-xylene, no such higher chlorinated products could be obtained in the present investigation. The course of the reactions during the two chlorinations again reveals the influence of the phenyl group in a remarkable manner. In the derivatives of phenyldihydroresorcinol the group $\cdot CCl{:}CH\cdot CCl_2\cdot$ (compounds II and V), although unsaturated, does not further combine with chlorine, whereas in the corresponding derivatives of dimethyl-

dihydroresorcinol further chlorination readily occurs, producing more highly chlorinated derivatives. Since the transformation from the hydroaromatic series yields diphenyl derivatives with substituents in only one of the two rings, such reactions serve as a convenient method for the preparation of diphenyl derivatives of this type.

The separation of the chlorodiphenyls (III) and (VI) obtained as described above is conveniently effected by regulated oxidation with chromic and acetic acids, which converts the dichlorodiphenyl into 3 : 5-dichlorobenzoic acid : the stability of the dipbenyl nucleus to oxidation by chromic acid is increased by the introduction of negative substituents, even although these are all in the same ring. A separation may also be effected by means of their nitro-derivatives.

Nitration of 3 : 5-dichlorodiphenyl gives chiefly 3 : *5-dichloro-4'-nitrodiphenyl* (VII) with a smaller quantity of 3 : *5-dichloro-2'-nitrodiphenyl* (VIII). On prolonged boiling (16 hours) with chromic and acetic acids the former gives a small quantity of *p*-nitrobenzoic acid and 3 : 5-dichloro-2'-nitrodiphenyl partly decomposes completely and partly remains unattacked. That in both compounds the nitro-group is in the ring not containing the chlorine atoms is shown by (*a*) oxidation of the corresponding *amines* (IX and X) giving 3 : 5-dichlorobenzoic acid and (*b*) the chlorine atoms being inert towards piperidine (see Le Fèvre and Turner, J., 1927, 1113; this vol., p. 247). The identity of 3 : 5-dichloro-4'-nitrodiphenyl was proved by reduction and conversion of the base into a *trichlorodiphenyl* (XI), m. p. 88°, which was identical with the compound obtained by the elimination of the amino-group from 3 : 5 : 4'-trichloro-4-aminodiphenyl (XIII). The isomeric dichloronitrodiphenyl gave a *trichlorodiphenyl* melting at 58° (XII).



Nitration of 2 : 3 : 5-trichlorodiphenyl readily gives a mono-itro-compound which, owing to its exceptional stability towards ·xidation by chromic acid and its inertness towards piperidine, is egarded as 2 : 3 : 5-*trichloro-4′-nitrodiphenyl.*

These results of substitution are in agreement with the tentative ules that have been proposed for the orientation of substituents n the diphenyl series (Scarborough and Waters, J., 1926, 557; 3lakey and Scarborough, J., 1927, 3000).

EXPERIMENTAL.

Action of Phosphorus Pentachloride on Phenyldihydroresorcinol.— ʰhenyldihydroresorcinol (94 g.; 1 mol.) was suspended in 200 c.c. of lry chloroform, and phosphorus pentachloride (220 g.; in excess of ! mols.) gradually added; after an hour the reaction was completed ıy gentle warming. The chloroform was removed under reduced ıressure, and the residue poured on ice and extracted with ether. ʳrom the extract, washed with 10% sodium hydroxide solution and rith water and dried, 3 : 5-*dichloro*-1-*phenyl*-$\Delta^{2:4}$-cyclo*hexadiene* I) (70 g.) was obtained as a colourless oil, b. p. 156°/10 mm. Found: Cl, 31·2. $C_{12}H_{10}Cl_2$ requires Cl, 31·55%), and also : 5-dichlorodiphenyl, b. p. 166°/10 mm., m. p. 36° (Found: 'l, 31·8. Calc.: Cl, 31·8%).

Action of Chlorine on 3 : 5-*Dichloro*-1-*phenyl*-$\Delta^{2:4}$-cyclo*hexadiene.* –(1) *At room temperature.* Chlorine was slowly passed for 2 hours ıto a solution of 65 g. of 3 : 5-dichloro-1-phenyl-$\Delta^{2:4}$-*cyclo*-exadiene in 50 c.c. of dry chloroform cooled by water. After the volution of hydrogen chloride had ceased, the chloroform was emoved on a boiling water-bath, and the residue left for several .ays in a vacuum over solid sodium hydroxide. The solution was istilled under reduced pressure and two fractions were collected: i) b. p. 164—166°/9 mm. (52 g.) and (ii) b. p. 166—200°/9 mm. 14 g.). The main fraction solidified in a freezing mixture, and rystallisation from cold alcohol gave 3 : 5-dichlorodiphenyl as now-white needles which, alone or mixed with the synthetic product btained from 3 : 5-dichloro-2-aminodiphenyl (Scarborough and Vaters, J., 1927, 89), melted at 36°. Oxidation with chromic and cetic acids gave 3 : 5-dichlorobenzoic acid (m. p. 183°). Fraction ii) was added to the fractions obtained from the chlorination at he higher temperature.

(2) *In hot solution.* A rapid stream of chlorine was passed into hot solution of 3 : 5-dichloro-1-phenyl-$\Delta^{2:4}$-*cyclo*hexadiene (56 g.) ı dry chloroform (60 c.c.) until the copious evolution of hydrogen hlorido had ceased and the solution had regained normal temper-ture. After removal of the chloroform, the oily residue was dis-

tilled under reduced pressure and three fractions were collected, b. p. 170—175°, 175—180°, and 180—200°/10 mm., respectively. The fraction of b. p. 170—175°/10 mm. (35 g.) gave mainly 3 : 5-dichlorodiphenyl on redistillation. The fraction of b. p. 180—200°/10 mm. was boiled for 6 hours with an excess of chromic acid in glacial acetic acid solution. The solid obtained by dilution with water, after crystallising several times from aqueous alcohol, gave 2 : 3 : 5-trichlorodiphenyl in small, white needles which, alone or mixed with the trichlorodiphenyl obtained from 3 : 5-dichloro-2-aminodiphenyl (Scarborough and Waters, *loc. cit.*) by the Sandmeyer reaction, melted at 41° (Found : Cl, 41·4. $C_{12}H_7Cl_3$ requires Cl, 41·35%). A small quantity of 3 : 5-dichlorobenzoic acid was obtained from the mother-liquor. Treatment of the fraction of b. p. 175—180°/10 mm. in like manner also gave 2 : 3 : 5-trichlorodiphenyl.

Action of Nitric Acid on the Fraction of b. p. 175—180°/10 *mm.*—5 G. of the fraction, dissolved in glacial acetic acid, were gradually treated with 25—30 c.c. of nitric acid (*d* 1·51). The solution, after being warmed, was poured into water and the solid which separated was crystallised repeatedly from alcohol. A small quantity of 2 : 3 : 5-trichloro-4′-nitrodiphenyl and mainly 3 : 5-dichloro-4′-nitrodiphenyl were isolated from the less soluble portions, and concentration of the mother-liquor yielded a small quantity of 3 : 5-dichloro-2′-nitrodiphenyl.

Nitration of 3 : 5-*Dichlorodiphenyl.*—5 G. of 3 : 5-dichlorodiphenyl, dissolved in 12 c.c. of glacial acetic acid, were nitrated by the gradual addition of 50 c.c. of a mixture of equal volumes of fuming nitric and glacial acetic acids. The solid which separated after the addition of water was crystallised from alcohol, 3 : 5-*dichloro-*4′-*nitrodiphenyl* being obtained in small, faintly yellow needles, m. p. 146° (Found : Cl, 26·6. $C_{12}H_7O_2NCl_2$ requires Cl, 26·5%). 3 : 5-*Dichloro-*2′-*nitrodiphenyl* separated from the mother-liquor and on recrystallisation was obtained in needles, m. p. 75° (Found : Cl, 26·4%).

3 : 5-*Dichloro-*4′-*aminodiphenyl.*—2 G. of 3 : 5-dichloro-4′-nitrodiphenyl, dissolved in 30 c.c. of alcohol, were reduced with 10 g. of stannous chloride in 10 c.c. of concentrated hydrochloric acid. The mixture was heated for several hours on the water-bath and, after evaporation of the alcohol, the *base*, liberated by addition of sodium hydroxide solution, was extracted with ether; it crystallised from aqueous alcohol in flat acicular plates, m. p. 124° (Found : Cl, 29·9. $C_{12}H_9NCl_2$ requires Cl, 29·8%). 3 : 5-*Dichloro-*4′-*acetamidodiphenyl*, prepared from the base in the usual manner, crystallised from alcohol in small white needles, m. p. 188° (Found : Cl, 25·5. $C_{14}H_{11}ONCl_2$ requires Cl, 25·4%).

3 : 5-*Dichloro-2'-aminodiphenyl*, obtained from the corresponding nitro-compound by reduction with stannous chloride in alcoholic solution as described above, separated from aqueous alcohol in needles, m. p. 74° (Found : Cl, 29·8%). Acetylation gave 3 : 5-*dichloro-2'-acetamidodiphenyl*, which crystallised from alcohol in small acicular plates, m. p. 163° (Found : Cl, 25·6%).

3 : 5 : 4'-*Trichlorodiphenyl*.—4 G. of 3 : 5-dichloro-4'-aminodiphenyl were diazotised in hydrochloric acid solution at 0° and then treated with cuprous chloride solution in the usual manner. On distillation with steam 3 : 5 : 4'-*trichlorodiphenyl* was obtained which separated from alcohol in white glistening needles, m. p. 88° (Found : Cl, 41·3. $C_{12}H_7Cl_3$ requires Cl, 41·35%).

3 : 5 : 2'-*Trichlorodiphenyl*.—4 G. of 3 : 5-dichloro-2'-aminodiphenyl were diazotised and treated as described above. The product crystallised from alcohol in faintly yellow needles, m. p. 58° (Found : Cl, 41·4%).

Nitration of 2 : 3 : 5-*Trichlorodiphenyl*.—Fuming nitric acid was gradually added to a solution of 2 : 3 : 5-trichlorodiphenyl in glacial acetic acid. 2 : 3 : 5-*Trichloro-4'-nitrodiphenyl*, obtained by diluting the solution with water, crystallised from alcohol in long, yellow needles, m. p. 155° (Found : Cl, 35·1. $C_{12}H_6O_2NCl_3$ requires Cl, 35·2%).

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CCCLXIX.—*A Study in the Formation of Gels. Vulcanised Oils.*

By B. C. J. G. KNIGHT and P. STAMBERGER.

IT has been shown (Stamberger, *Rec. trav. chim.*, 1927, **46**, 837; 1928, **47**, Oct. 15) that an insoluble, tough, elastic substance is formed by heating triolein with sulphur. The process may be divided into three stages: (1) Combination of the triolein with sulphur; (2) polymerisation of these molecules to double molecules; (3) further polymerisation giving the elastic substance. From the reaction mixture may be separated an acetone-soluble portion corresponding to stage 1, and a benzene-soluble portion (stage 2). The remaining highly polymerised product is insoluble.

Further information has now been obtained on the processes concerned by two methods: (*a*) *X*-ray examination of the products; (*b*) examination of the behaviour of the soluble products when spread as thin films on a water surface.

EXPERIMENTAL.

For convenience the details of the various products which hav been examined are given in Table I.

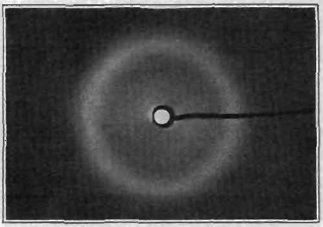
TABLE I.

Substance.	*d.*	Sulphur content, %.	No. of S atoms per mol.	State of aggregation.	*M*, calc.	Diameter of circle in *X*-ray diagram.
Triolein.	0·920	—	—	Liquid.	884	28·06 mm
Vulcanised triolein:						
Acetone-soluble.	1·03	16·6	4— 5	Very viscous liquid.	1044 / 1076	27·74
Benzene-soluble, I.	1·04	16·4	10—12	Viscous, pasty liquid.	2088 / 2152	27·68
Benzene-soluble, II.	1·04	16·4	10—12	Slightly elastic, sticky solid.	2088 / 2152	28·10
Benzene-soluble, III, dissolved by heating not higher than 60°.	—	16·4	—	More elastic than I and II.	7000 (cryoscopic)	—
Insoluble, elastic solid.	—	16·3	—	Tough, elastic substance.	—	28·10
Oleic acid.	0·891	—	—	Oil.	282	—
Fatty acids from saponification of vulcanised triolein.	0·071	13·7	3— 4	Very viscous liquid.	937 / 969	— / —

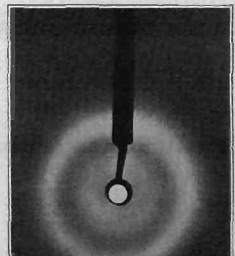
The *X*-ray diagrams were obtained by the method described b Katz (*Z. Physik*, 1927, **45**, 100) with Cuα rays. All the product gave circles of the same diameter (Figs. 1*a* and *b*), which is calculate for a distance of 40 mm. between the substance and the photographi plate, and shown in Table I; these circles indicate an amorphou structure. The *X*-ray examination did not show any change i the molecules in the different stages of the reaction.

Unimolecular Films.—The soluble products and the sulphur containing oleic acid obtained by cold saponification have bee found to give unimolecular films of the expanded type when sprea on water. The films of these substances have been studied b using the apparatus and technique of Adam (*Proc. Roy. Soc.*, 192 *A*, **110**, 423). Dilute benzene solutions of known concentratio of the several products were prepared. Known weights of thes solutions were placed upon a clean water surface in a Langmuir Adam trough by means of a capillary drop-pipette. The forc of compression acting on the film when the area was diminishe was measured by means of Adam's torsion apparatus (*loc. cit.*).

The results of the measurements are given in Figs. 2 and where the compressing force (*F* in dynes/cm.) is plotted agains the thickness of the film (in Ångström units). The molecula weights of the substances cannot be accurately determined, a they are not sharply defined chemical compounds. We have pr ferred, therefore, to plot the thickness of the film as calculate from its area, the weight of substance, and its specific gravit (*d* in Table I), rather than the area per molecule. In Table II ar collected the values for the dimensions of the molecules derive



X-Ray diagram of triolein.
FIG. 1*a*.



X-Ray diagram of vulcanised triolein.
FIG. 1*b*.

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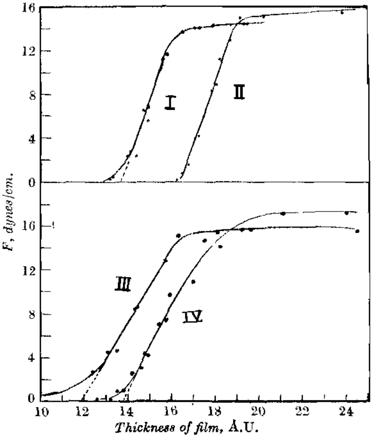
from the curves. The areas per molecule have been calculated approximately, assuming theoretical molecular weights derived from the sulphur content and the cryoscopic measurements.

Fig. 2.



Curve I. Benzene-soluble part, I and II, 16°.
,, *II. Benzene-soluble part, III*, 18°.
,, *III. Triolein.*
,, *IV. Acetone-soluble part*, 16°.

Table II.

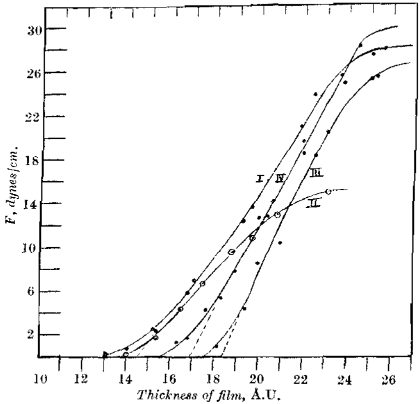
Substance.	Thickness in film at zero pressure.	Temp.	Area per molecule, sq. Å.U., at zero pressure.
Triolein	13·0 Å.U.	16°	132
Acetone-sol.	13·9	16	125
Benzene-sol., I and II	13·9	16	260
Benzene-sol., III	16·3	18	—
Oleic acid	13·8	16 and 1	35
Sulphurised oleic acid	16·9	16	96
Sulphurised oleic acid	18·5	1	86

Discussion.

It is of interest to correlate the observations made in the above experiments with the physical properties of these substances and with the appearance of elastic properties.

The combination with sulphur in the first part of the reaction does not alter the mode of orientation, and only very slightly affects the dimensions of the molecule. The film of the acetone-soluble product is about 1 Å.U. thicker at zero pressure than that of triolein, indicating that the hydrocarbon chains are tending to be oriented more nearly perpendicular to the water surface. The position of the sulphur in the molecule is not definitely determined. Most probably it is in a chain connecting the double bonds of the

FIG. 3.



Curve I. Oleic acid at 1°.
,, II. Oleic acid at 16°.
,, III. Sulphurised oleic acid at 1°.
,, IV. Sulphurised oleic acid at 16°.

adjacent oleic acid chains, since after saponification most of the sulphur is still attached to the fatty acids. About 16·5% of the sulphur is found with the glycerol after saponification, not as inorganic sulphur. Cryoscopic determinations on these sulphur-containing fatty acids show that they are still combined in groups of three. The acetone-soluble product of the first stage of the reaction is a viscous fluid substance having no elastic properties.

In the second stage of the reaction the molecules polymerise first to double molecules. This is the benzene-soluble part, and is a viscous, pasty fluid substance, slightly elastic. This substance

changed to a still more elastic sticky solid on standing for 3—4 months in a closed weighing bottle. This change could be accelerated by heating or by irradiation with ultra-violet light. An elastic solid was also obtained by keeping the benzene-soluble part under water or acetone for several days. These solid products only swelled in benzene at room temperature, but could be dissolved on continued boiling. It appears probable that the highly polymerised or aggregated molecules of the elastic solid obtained from the benzene-soluble part in this manner had been broken down by the hot solvent to double molecules. All these benzene-soluble products gave the same results on spreading on water. The thickness of the film was about the same as that of the acetone-soluble part. The area per molecule at zero pressure, calculated from the theoretical molecular weight (cryoscopic measurements and sulphur content), was twice that of the acetone-soluble part. This indicates that the double molecules are formed by the joining of two molecules side by side. The polar glyceryl groups are apparently unaltered, since the orientation is unaffected.

By careful heating with benzene for 2 days at a temperature not higher than 60°, the elastic polymerised product obtained from the benzene-soluble part (I) (by standing for 3—4 months at room temperature) could be completely dissolved. Cryoscopic measurement showed a very high molecular weight, at least 7000. This product (benzene-soluble, III) gave, on spreading, a film 16·3 Å.U. thick—again a unimolecular film. The slightly greater thickness of this film may be due to the polymerisation to larger groups of molecules (at least 7) causing closer packing of the fatty-acid chains. The form of the compression curve at low pressures shows that the film is there much less expanded (see Fig. 2).

The same elastic polymerised product was nearly completely dissolved on being kept under benzene at room temperature for 14 days. This solution gave no freezing-point depression even at a concentration of 7%. Accurate figures for the film thickness cannot be given owing to traces of substance being undissolved. Several measurements gave values for the thickness of 17 Å.U. at zero pressure, showing at least that the film is still one molecule thick. These measurements show that the higher molecular aggregates are formed by the linking of several molecules side by side, repeating the method of formation of the double molecules.

After saponification the elastic properties of the solid disappear. The sulphurised oleic acid is a viscous liquid. Moreover, no elastic substance could be obtained by heating oleic acid with sulphur. The sulphurised acids obtained by both methods gave films of the

same thickness, a little thicker than oleic acid. Since the fatty acids are in groups of three after saponification of both the benzene-soluble part and the elastic solid (see Stamberger, *loc. cit.*), it seems that the polymerisation is not caused by sulphur linking together hydrocarbon chains of adjacent molecules, but rather suggests that the glyceryl portion of the molecules takes part in the combination to give the elastic solid. If this is broken by saponification, the elastic properties disappear, although the fatty acids are still held together in groups of three.

The effect of lowering the temperature is interesting (see Fig. 3). A change from 16° to 1° has very little effect on the area of the oleic acid film, but this may be subjected to a somewhat higher pressure at the lower temperature before collapsing. The oleic acid film at 0° is still considerably above its temperature of transition from the expanded to condensed type of film as shown by Adam (*Proc. Roy. Soc.*, 1926, *A*. **112**, 362). On the other hand, an equal lowering of temperature causes a considerable decrease in the film of the sulphurised oleic acid. It is evident that at 1° the latter film is much nearer to its transition temperature than is oleic acid : it is approaching the behaviour of the corresponding saturated fatty acid film. The sulphurised oleic acid is less compressible than oleic acid. These differences in behaviour are undoubtedly due to the fact that in the former substance the fatty-acid chains are held together by sulphur, the double bonds being partially saturated. The molecules are thus oriented more in the manner of a condensed film.

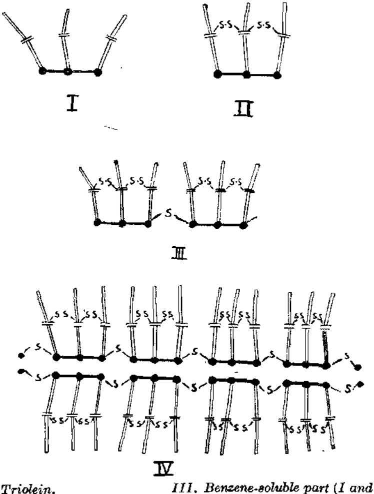
It is now possible to suggest a theory of the formation of the final insoluble, elastic substance. The double molecules of the benzene-soluble substance have been shown to be formed by the linking together, side by side in a definite orientation, of two single molecules. The more highly polymerised product containing at least 7 molecules (benzene-soluble, III, fairly elastic) is formed by the linking of further molecules in the same manner. This combination is between the glyceryl parts of the molecules. It seems probable, therefore, that in the final insoluble elastic product there would be long chains of molecules oriented with respect to one another side by side, with their hydrocarbon chains more or less parallel, combined by a repetition of this process.

This conception of the structure leading to the formation of the insoluble elastic substance is illustrated by the diagrams in Fig. 4. On this hypothesis, the slow change of the viscous fluid to an elastic solid may be explained by the slow orientation of the molecules to give long chains. The acceleration by heating and by ultra-violet irradiation is then due to the increased number of effective collisions,

and therefore of opportunities for linking and orientation, under these conditions.

McBain has reached somewhat similar conclusions in the case of the formation of soap jellies from solution (Alexander, "Colloid Chemistry," p. 141); he says "The conclusion seems inevitable that the actual colloidal particles are the same in solution and in the true jelly, but that in the jelly the particles of neutral colloid are

FIG. 4.



I. Triolein. *II. Acetone-soluble part.* *III. Benzene-soluble part (I and II).* *IV. The elastic solid.*

linked together probably to form innumerable ultramicroscopic filaments."

In a later paper (*J. Amer. Chem. Soc.*, 1927, **49**, 2230), in order to explain the observed surface concentration found to be in excess of that required for a complete unimolecular film, McBain has put forward a theory of chains of oriented molecules extending downwards from the surface of solutions of non-electrolytes. He points out that the effect of finely ground fillers upon the strength and

resiliency of rubber may be explained by this conception. The extensive surface of the finely ground filler has the rôle of orienting molecules in contact with it, and the chain effect extends with diminishing intensity into the surrounding rubber. Our view, that the increase of elasticity in the vulcanisation of triolein is due to a vectorial orientation of molecules, is in agreement with McBain's theory.

Recently, Sheppard and Keenan (*Nature*, 1928, **121**, 982) have given some interesting data for the spreading of cellulose esters on mercury. In order to explain the thinness of the films they suggest that a polymeric chain or sheet is formed one molecule thick. For this type of molecule the orientation is apparently with the chains parallel to the surface.

Summary.

1. The entrance of sulphur into triolein in vulcanisation does not change its orientation on water, and only very slightly alters the dimensions of the molecule. Elastic substances can be obtained from this product.

2. Measurements of thin films show that, in the polymerisation to such elastic substances, the molecules are linked side by side in a definitely oriented manner in long chains.

3. This work provides a basis for a theory of elastic formation in a solid.

Our best thanks are due to Prof. F. G. Donnan for criticisms and suggestions, and to Prof. J. C. Drummond for allowing the work on the films to be carried out in his department. This opportunity is taken of thanking Dr. N. K. Adam for much help when the torsion apparatus was under construction. Acknowledgment is also made to the Department of Scientific and Industrial Research for a grant held by one of us (B. C. J. G. K.).

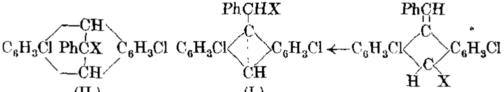
DEPARTMENTS OF BIOCHEMISTRY AND OF PHYSICAL CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, August 2nd*, 1928.]

CCCLXX.—*Transannular Anionotropic Migrations.*

By JAMES WILFRED COOK.

IT has been shown (Barnett, Cook, and Matthews, *Ber.*, 1927, **60**, 2353) that the monobromo-derivative of 1 : 5-dichloro-9-benzyl-anthracene exhibits dual properties inasmuch as it yields two distinct series of hydroxy-, acetoxy-, methoxy-, and ethoxy-compounds by suitable treatment, *viz.*, (*a*) yellow and fluorescent

compounds which are represented by formula (I) and (*b*) colourless and non-fluorescent isomeric compounds, obtained when the hydrogen bromide formed by the reaction is removed as rapidly as it is produced, which pass into their yellow isomerides under the influence of hydrogen ions. Moreover, both hydroxy-compounds are converted by hydrogen bromide into the original bromo-compound. Barnett and Matthews (*loc. cit.*) suggested tentatively that the colourless compounds have endocyclic structures (II), whereas the author (Cook, *Ber.*, 1927, **60**, 2366) regarded this as improbable and assigned a benzylidene structure (III) to the colourless compounds, postulating a migration of X to account for the interconversion of compounds of the two series :



(II.) (I.) (III.)

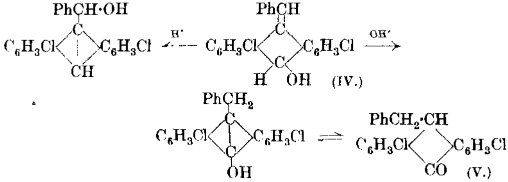
The present communication deals with attempts to decide between structures (II) and (III); it is not claimed that the endocyclic structure (II) is definitely disproved, but there is much new evidence to substantiate structure (III) for the colourless compounds.

The analogy existing between the tautomeric system contained in a 9-alkyl derivative of anthracene (the " bridge " being regarded as equivalent to an ethylenic bond) and the simpler 3-carbon system has been established by the interconversion of 1 : 5-dichloro-10-phenyl-9-methylanthracene and the pseudo-tautomeric methylene compound (Barnett and Cook, *Ber.*, 1928, **61**, 314), and the postulated change (III)$\longrightarrow$(I) is then seen to be comparable with the bromine migrations in simpler conjugated systems recently studied by Farmer, Laroia, Switz, and Thorpe (J., 1927, 2937) * and Farmer, Lawrence, and Thorpe (this vol., p. 729) * and with the mobile anion tautomeric changes described by Burton and Ingold (this vol., p. 904).*

The suggestion was made tentatively (Cook, *loc. cit.*) that the rearrangement in the anthracene series is preceded by ionic dissociation, and this mechanism has been confirmed in the case of the α-phenylallyl system hy the experiments of Burton (this vol., p. 1650). The order of mobility of the anions (Br>OAc> OH or OR), identical with that observed by Burton and Ingold in their compounds, is further evidence of the ionic nature of

* Other examples of mobile anion tautomerism may be found from the references given in these papers.

the migrations and it is also significant that, whereas hydrogen ions promote hydroxyl migration in the colourless hydroxy-compound (IV), hydroxyl ions bring about hydrogen migration. The 1 : 5-dichloro-9-benzylanthrone (V) resulting from the latter change was identified by direct comparison with an authentic sample and also by conversion into 1 : 5-dichloro-9-benzyl-10-phenylanthracene by treatment with magnesium phenyl bromide, followed by dehydration of the resulting carbinol.

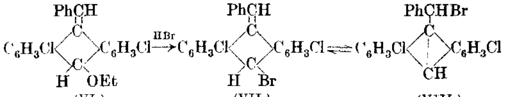


This prototropic change, effected by brief boiling with sodium hydroxide solution, is comparable with analogous changes in open-chain systems (Burton and Ingold, *loc. cit.*).

More definite evidence that the substituent group in the colourless compounds is attached to the 10-carbon atom of the anthracene ring is afforded by an experiment carried out with the 1 : 5-diehloro-10-ethoxy-9-benzylidene-9 : 10-dihydroanthracene * (VI) prepared by Barnett (unpublished work) by the action of magnesium benzyl chloride on 1 : 5-dichloroethoxyanthrone and dehydration of the resulting dihydroanthranol. This ethoxy-compound (VI) is different from the colourless ethoxy-compound previously prepared (Barnett, Cook, and Matthews, *Ber.*, 1927, **60**, 2361) and is presumably its geometrical isomeride. It has not been possible to effect its direct conversion into the ω-ethoxy-compound, the reaction with alcoholic hydrogen chloride being slow and incomplete. This difference in migratory power between the two geometrical isomerides is curious and may be compared with a similar difference observed with the 1 : 2-dibromides of the two stereoisomeric hexatrienes (Farmer, Laroia, Switz, and Thorpe, J., 1927, 2942). The desired conversion was obtained through the bromo-compound, replacement of the ethoxy-group by the more mobile bromine atom by treatment of (VI) with hydrogen bromide leading to the same monobromo-

* I am indebted to Dr. E. de Barry Barnett for his kindness in giving me a few grams of this benzylidene compound.—J. W. C.

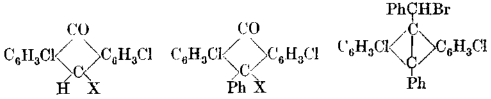
compound (VII) as was obtained by bromination of 1 : 5-dichloro-9-benzylanthracene.



(VI.) (VII.) (VIII.)

The inversion of geometrical configuration evidently proceeds through the tautomeric phase (VIII), it having been shown already that (VIII) cannot be isolated owing to the ease with which it passes into its isomeride of the "colourless" type (Barnett, Cook, and Matthews, *loc. cit.* Compare Barnett, Cook, and Ellison, this vol., p. 889).

It should be possible to obtain evidence of structure (III) for the colourless compounds by oxidation to the anthrone derivative (IX).

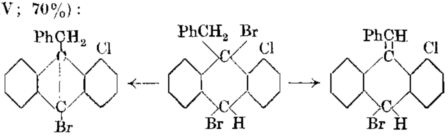


(IX.) (X.) (XI.)

As long as there is a mobile hydrogen atom this course is not practicable on account of the ease with which the enol is oxidised. If the mobile hydrogen atom is replaced by a phenyl group, enolisation is no longer possible, so that the phenylanthrone derivative (X) should be capable of isolation from the oxidation products. With this object in view the preparation of a series of derivatives of 1 : 5-dichloro-9-benzyl-10-phenylanthracene was initiated. The substance gave a reactive *monobromo*-derivative, but the *hydroxy*- and *ethoxy*-compounds obtained from it by treatment with aqueous acetone and ethyl alcohol, respectively, in the presence of calcium carbonate were obviously of the "yellow" and fluorescent type, and this, coupled with the deep orange colour of the bromo-compound, renders it fairly certain that the latter has structure (XI). The influence of replacement of hydrogen by phenyl on the equilibrium of the anionotropic system is explicable on the electronic hypothesis of Burton and Ingold and steric influences would operate in the same direction.

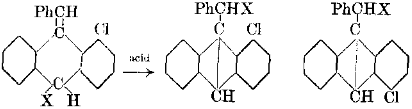
The problem was attacked from another standpoint by attempting the preparation of colourless series of derivatives from 1-*chloro-9-benzylanthracene* and 4-*chloro-9-benzylanthracene*. If the endo-

cyclic structure were correct, the molecule would be symmetrica and these two series of compounds would have identical structure (XII). Now, although 1 : 5-dichloro-9-benzylanthracene gives a reactive bromo-derivative, 9-benzylanthracene yields only th 10-bromo-derivative (Cook, J., 1926, 2161. Compare *Ber.*, 1927 **60**, 2366), so that the first possible pitfall was that a single α-chlorin atom might fail to have the necessary influence on the bromination Actually, 1-chloro-9-benzylanthracene on bromination yielded a very unstable dibromide which decomposed into a mixture of the *10-bromo*-compound (XIII; 30%) and the *benzylidene* compound (XIV; 70%):



(XIII.) (XIV.)

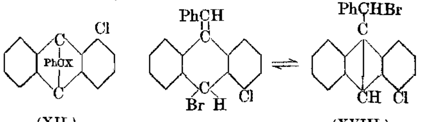
From the reactive bromo-compound (XIV) derivatives were obtained of both "colourless" (XV) and "yellow" (XVI) types.



(XV.) (XVI.) (XVII.)

(X = OH, O·COMe or OR.)

The unstable dibromide of 4-chloro-9-benzylanthracene gave only the reactive *bromo*-compound, but this passed into "yellow" *substitution products (XVII) even in the presence of calcium* carbonate and it seems fairly certain in this case that the ω-bromo-compound is the stable tautomeride, so that the bromo-compound has structure (XVIII).

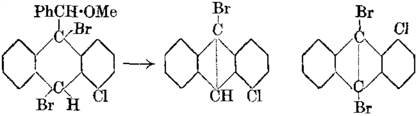


(XII.) (XVIII.)

The steric effect of the α-chlorine atom can account for these differences between the 1-chloro- and the 4-chloro-derivatives of 9-benzyl-

anthracene. The non-formation of colourless derivatives of the 4-chloro-compound has prevented definite refutation of the endocyclic structure. It is certain, however, that the endocyclic compounds were not formed as intermediate products in the preparation of the ω-derivatives of 4-chloro-9-benzylanthracene, since the latter substances were quite different from the isomeric ω-derivatives obtained from 1-chloro-9-benzylanthracene.

The proof of the structure assigned to the "yellow" compounds is similar to that previously advanced in the case of the 1 : 5-dichloro-compounds. For instance, 4-chloro-ω-methoxy-9-benzylanthracene gave an unstable dibromide which spontaneously decomposed into benzaldehyde and 4-chloro-9-bromoanthracene (XIX):



(XIX.) (XX.)

This new bromo-compound was identical with the substance obtained by Barnett and Matthews (*Rec. trav. chim.*, 1924, **43**, 535) by thermal decomposition of α-chloroanthracene dibromide, and the present result determines the orientation of their compound. 4-Chloro-9-bromoanthracene is stable in the presence of excess of bromine, thus resembling 1 : 5-dichloro-9-bromoanthracene (Barnett, Cook, and Matthews, *loc. cit.*), but differing from 9-bromoanthracene itself which is readily brominated. 1-Chloro-9-bromoanthracene appears to resemble 9-bromoanthracene, since it was not isolated from the decomposition products of the dibromide of 1-chloro-ω-methoxy-9-benzylanthracene, only the dibromo-compound (XX) being obtained. The bromine necessary for bromination of the monobromo-compound was evidently obtained by partial loss of bromine from the original dibromide of the methoxybenzyl compound. The difference in behaviour between the isomeric α-chloro-9-bromoanthracenes may again be attributed to the steric effect of the α-chlorine atom, provided it is assumed that bromination is preceded by 9 : 10-addition of bromine, as is certainly the case with the bromination of many other anthracene derivatives.

The ω-*methoxy*-derivative of 1-chloro-9-benzylanthracene was converted by hydrogen bromide into the "colourless" bromo-compound (XIV), so that, as in the 1 : 5-dichloro-series, the "benzylidene" bromo-compound is the stable tautomeride, whereas with the hydroxy-, *acetoxy*-, and alkoxy-derivatives the ω-structure is

the more stable. This curious difference, in conjunction with th fact that the ω-bromo-derivative of 4-chloro-9-benzylanthracene i the stable tautomeride, is doubtless due to steric factors. Thus the omega structure is normally the stable type, but the pre sence of the chlorine atom in position 1 hinders the attachmen of such a bulky group as bromine to the ω-carbon atom. It i perhaps significant that the bromine atom tends to take up position as remote as possible from the α-chlorine atom (XIV an XVIII) and it may be that this is partly determined by polar factors

It has been shown (Cook, J., 1926, 2161) that the action of exces of bromine on 10-bromo-9-benzylanthracene results in addition t one of the *Bz* rings with the formation of a tetrabromide. Whe 1-chloro-10-bromo-9-benzylanthracene (XIII) was treated wit excess of bromine a tetrabromide was not obtained, the only pro duct isolated being 4-chloro-9-bromoanthracene (XIX). At pre sent it is not proposed to discuss this apparent replacement of benzyl group by a hydrogen atom by means of bromine.

EXPERIMENTAL.

Prototropic Rearrangement of 1 : 5-*Dichloro*-10-*hydroxy*-9-*benzyl idene*-9 : 10-*dihydroanthracene* (IV).—The hydroxy-compound (5 g. was added to a solution of alcoholic sodium hydroxide prepared fron sodium (5 g.) and 95% alcohol (125 c.c.). A deep blood-red colou was developed on boiling and the boiling was continued for ½ hour The resinous product, obtained by dilution with water, was recrystal lised twice from ethyl acetate and then formed colourless crystal (1·5 g.) which melted at 169—170° alone or when mixed wit 1 : 5-dichloro-9-benzylanthrone (V). The identification was com pleted by treatment with magnesium phenyl bromide, dehydratio of the resulting dihydroanthranol yielding 1 : 5-dichloro-9-benzyl-10-phenylanthracene, m. p. 211—212° (alone or mixed with a authentic sample).

The corresponding ethoxy-compound was recovered unchanged after boiling for 7 hours with alcoholic sodium hydroxide.

Action of Hydrogen Bromide on 1 : 5-*Dichloro*-10-*ethoxy*-9-*benzyl-idene*-9 : 10-*dihydroanthracene* (VI).—This ethoxy-compound (m. p. 170°; 1·5 g.), one of the products of the action of magnesium benzyl chloride on 1 : 5-dichloro-10-ethoxy-9-anthrone (see foot-note on p. 2800) and shown to be different from the original colour-less ethoxy-derivative of 1 : 5-dichloro-9-benzylanthracene, was dissolved in toluene (10 c.c.), and hydrogen bromide passed through the boiling solution for 20 minutes. After cooling and dilution with light petroleum, crystals separated which, after recrystallisation from benzene–light petroleum, melted at 180—182° alone or mixed

with the monobromo-derivative *obtained from* 1 : 5-*dichloro*-9-benzylanthracene. The identification of the bromo-compound was completed by its conversion into the original colourless ethoxy-compound by means of alcohol in the presence of calcium carbonate. The new ethoxy-compound of Barnett was thus indirectly converted into its geometrical isomeride.

Derivatives of 1 : 5-*Dichloro*-9-*benzyl*-10-*phenylanthracene*.

(*a*) ω-*Bromo-derivative* (XI).—A solution of 1 : 5-dichloro-9-benzyl-10-phenylanthracene (16 g.) in carbon disulphide (100 c.c.) was treated slowly at the ordinary temperature with bromine (2 c.c.). After 3 hours the solvent was removed by distillation; the residual resin, when treated with ether, became solid. The product crystallised from benzene–ether in orange crystals, m. p. 179—180° (Found : Cl + Br, 30·6. $C_{27}H_{17}Cl_2Br$ requires Cl + Br, 30·7%).

(*b*) ω-*Hydroxy-derivative*.—The bromo-compound (XI; 5 g.) was heated on the water-bath for 4 hours with calcium carbonate (1 g.) and acetone (60 c.c.) diluted with water (15 c.c.). The product was recrystallised twice from benzene–light petroleum and twice from benzene–alcohol and then formed canary-yellow nodules, m. p. 189—191° (Found : C, 75·1; H, 4·3. $C_{27}H_{18}OCl_2$ requires C, 75·5; H, 4·2%). Solutions of the substance had a blue fluorescence.

(*c*) ω-*Ethoxy-derivative*.—The bromo-compound (XI; 5 g.) was heated on the water-bath for 2 hours with ethyl alcohol (50 c.c.). The crude product, m. p. 150—155°, was repeatedly crystallised from benzene–alcohol until it melted constantly at 173—174° (Found: C, 75·9; H, 4·85. $C_{29}H_{22}OCl_2$ requires C, 76·1; H, 4·8%). This *ethoxy*-compound formed glistening yellow leaflets, fluorescent in solution, and the same result was obtained when the reaction was carried out in the presence of calcium carbonate.

α-*Chloro*-9-*benzylanthracenes*.

1-*Chloro*-9-*benzylanthracene*.—1-Chloro-9-anthrone (30 g.), obtained by reducing α-chloroanthraquinone with aluminium and sulphuric acid (Eckert and Tomaschek, *Monatsh.*, 1918, **39**, 839; compare Barnett and Matthews, *J.*, 1923, **123**, 2550), was added slowly to a Grignard solution prepared from benzyl chloride (42 c.c.) and magnesium powder (9 g.), the solution being cooled in a freezing mixture. After 4 hours the suspension was poured on ice and ammonium chloride, the ethereal solution washed, and the ether removed by distillation. The viscous residue was treated with light petroleum, and the resulting solid (40 g.) twice recrystallised

from benzene–light petroleum (Found : C, 78·6 ; H, 5·4. $C_{21}H_{17}OC$ requires C, 78·6 ; H, 5·3%). *1-Chloro-9-hydroxy-9-benzyl-9 : 10-dihydroanthracene* forms a colourless crystalline powder, m. p. 126—127°. It was dehydrated by allowing its solution in acetic acid containing hydrochloric acid to stand over-night at the ordinary temperature. The resulting *1-chloro-9-benzylanthracene*, recrystallised from benzene–alcohol, formed pale yellow nodules, m. p. 119—120° (Found : C, 83·5 ; H, 5·05. $C_{21}H_{15}Cl$ requires C, 83·3 H, 5·0%).

4-Chloro-9-benzylanthracene was obtained in good yield in exactly the same way from 4-chloro-9-anthrone, prepared by reducing α-chloroanthraquinone with tin and hydrochloric acid (Barnett and Matthews, J., 1923, **123**, 2550). The crude dihydroanthranol was not purified but was converted into the chlorobenzylanthracene pale yellow needles from ethyl acetate–alcohol, m. p. 120° (Found Cl, 11·8. $C_{21}H_{15}Cl$ requires Cl, 11·7%).

Bromination. Each α-chloro-9-benzylanthracene (15 g.) was dissolved in carbon disulphide (50 c.c.) and the solution, cooled in a freezing mixture, was treated with bromine (2·5 c.c.). The bromine was taken up without evolution of hydrogen bromide and in each case a solid additive compound separated, which passed into solution with liberation of hydrogen bromide on warming to the ordinary temperature. After an hour the solvent was removed by distillation, the residual oil treated with light petroleum, and the resulting yellow solid collected and dried. The crude product from 1-chloro-9-benzylanthracene was obviously a mixture. A little was dissolved in boiling pyridine, alcohol added to the solution, and the resulting *1-chloro-10-bromo-9-benzylanthracene* (XIII) recrystallised from ethyl acetate ; it then formed yellow silky needles, m. p. 160° (Found : C, 66·0 ; H, 3·8. $C_{21}H_{14}ClBr$ requires C, 66·1 ; H, 3·7%). The constitution assigned to this bromo-compound depends upon its inert character, the substance being recovered unchanged after boiling for an hour with acetic anhydride containing sodium acetate or with alcoholic potassium hydroxide solution.

When the bromo-compound (XIII) was treated with excess of bromine (2 mols.) in carbon disulphide solution the bromine was slowly taken up with liberation of hydrogen bromide. After 12 hours the solvent was distilled off and the viscous residue triturated with a little ether. A solid remained which, recrystallised from ethyl acetate–alcohol, melted at 149—150° alone or mixed with 4-chloro-9-bromoanthracene (XIX) (Found : C, 57·3 ; H, 2·9. Calc. : C, 57·6 ; H, 2·75%).

1-Chloro-10-bromo-9-benzylidene-9 : 10-dihydroanthracene (XIV).— This was the chief product of the bromination of 1-chloro-9-benzyl-

anthracene, but could not be isolated from the crude mixture on account of its reactive nature. It was obtained, however, when hydrogen bromide was conducted through a boiling solution of 1-chloro-ω-methoxy-9-benzylanthracene (see below; 4 g.) in benzene (10 c.c.) for 15 minutes. The *bromo*-compound was obtained by adding light petroleum to the cooled solution and after recrystallisation from benzene–light petroleum formed almost colourless needles, m. p. 151—153° (Found: C, 66·1; H, 3·9. $C_{21}H_{14}ClBr$ *requires* C, 66·1; H, 3·7%). There can be no doubt that this compound was identical with the reactive bromo-compound present in the crude bromination mixture of 1-chloro-9-benzylanthracene, since by heating with methyl alcohol and calcium carbonate it was converted into the same colourless methoxy-compound as was obtained from the original bromination mixture. This mode of preparation of the pure bromo-compound (XIV) lends support to the hypothesis that in solution it is in tautomeric equilibrium with 1-chloro-ω-bromo-9-benzylanthracene (compare the equilibrium VII $\rightleftharpoons$ VIII).

4-*Chloro-ω-bromo-9-benzylanthracene* (XVIII) appeared to be the only isomeride formed by brominating 4-chloro-9-benzylanthracene. After recrystallisation from benzene–light petroleum it formed deep yellow nodules, m. p. 165—166° (Found: C, 66·2; H, 3·8. $C_{21}H_{14}ClBr$ requires C, 66·1; H, 3·7%).

"*Colourless*" *Derivatives of* 1-*Chloro*-9-*benzylanthracene.*

In all experiments with the bromo-compound (XIV) the crude mixture of isomerides obtained by brominating 1-chloro-9-benzylanthracene was used. The products (XV and XVI) obtained from (XIV) were usually very soluble in most solvents and remained in solution, the sparingly soluble 10-bromo-compound (XIII) being filtered off. The proportion of the latter compound isolated was consistently 30% of the crude mixture.

1 - *Chloro* - 10 - *hydroxy* - 9 - *benzylidene* - 9 : 10 - *dihydroanthracene* (XV; X = OH).—The mixed bromo-compounds (5 g.) were heated on the water-bath for 4 hours with acetone (60 c.c.), water (15 c.c.), and calcium carbonate (1 g.). After cooling, the 10-bromo-compound (XIII) was filtered off, the acetone distilled from the filtrate, and the resinous product recrystallised twice from benzene–light petroleum and once from toluene. The substance then formed a colourless crystalline powder, m. p. 185°, which, like the analogous 1 : 5-dichloro-compound (IV), gave an intense orange-red colour with boiling alcoholic potassium hydroxide solution (Found: C, 79·3; H, 4·8. $C_{21}H_{15}OCl$ requires C, 79·1; H, 4·7%).

The corresponding *acetoxy*-compound (XV; X = O·COMe) was

obtained when a solution of this hydroxy-compound (3 g.) in pyridine (10 c.c.) was treated for 6 hours at the ordinary temperature with acetic anhydride (5 c.c.). It formed colourless glistening crystals, m. p. 151—153°, from ethyl acetate–alcohol (Found : C, 76·3 ; H, 4·8. $C_{23}H_{17}O_2Cl$ requires C, 76·6 ; H, 4·7%).

1-*Chloro*-10-*methoxy*-9-*benzylidene*-9 : 10-*dihydroanthracene* (XV ; X = OMe).—The mixed bromo-compounds (3·5 g.) were heated on the water-bath for an hour with methyl alcohol (100 c.c.) in the presence of calcium carbonate (1 g.). After cooling, the filtered solution was concentrated and diluted with water. The resinous product was dried and recrystallised twice from benzene–light petroleum and then formed colourless glistening needles, m. p. 129—130°. Its solutions were non-fluorescent (Found : C, 79·3 ; H, 5·2. $C_{22}H_{17}OCl$ requires C, 79·4 ; H, 5·1%).

The corresponding ethoxy-compound could not be obtained solid.

"Yellow" Derivatives of 1-*Chloro*-9-*benzylanthracene*.

1-*Chloro*-ω-*methoxy*-9-*benzylanthracene* (XVI ; X = OMe).—The colourless methoxy-compound (above ; 0·8 g.) was heated on the water-bath for 1½ hours with methyl alcohol (15 c.c.) containing concentrated hydrochloric acid (1 c.c.). After cooling, the solid was collected and recrystallised from alcohol ; it then formed pale yellow needles, m. p. 135—136°. The solutions had a strong violet fluorescence and the m. p. was depressed by admixture with the original colourless methoxy-compound (XV) or with the methoxy-derivative obtained from 4-chloro-9-benzylanthracene (XVII) (Found : C, 79·4 ; H, 5·2. $C_{22}H_{17}OCl$ requires C, 79·4 ; H, 5·1%).

Bromine (0·3 c.c.) was added to a solution of this methoxy-compound (1·85 g.) in carbon disulphide (5 c.c.), cooled in a freezing mixture. The bromine was taken up but no hydrogen bromide was evolved. The addition of light petroleum resulted in the separation of a colourless solid, which was collected and, without purification, dissolved in boiling benzene. The solution became yellow and hydrogen bromide was evolved. After boiling for ½ hour, the solution was treated with alcohol and cooled, and the resulting crystals were recrystallised from ethyl acetate (Found : C, 45·3 ; H, 2·1. $C_{14}H_7ClBr_2$ requires C, 45·3 ; H, 1·9%). 1-*Chloro*-9 : 10-*dibromoanthracene* (XX) forms slender orange-yellow needles, m. p. 159—161°.

1-*Chloro*-ω-*acetoxy*-9-*benzylanthracene* (XVI ; X = O·COMe).—(*a*) A solution of the mixed bromo-compounds (5 g.) and sodium acetate (3 g.) in glacial acetic acid (35 c.c.) was boiled for an hour, cooled, and filtered from the 10-bromo-compound (XIII), and the

filtrate poured into water. The precipitate was collected, dried, and recrystallised from benzene–light petroleum and then from alcohol. The *acetoxy*-compound formed yellow prisms, m. p. 157—158°, and the m. p. was depressed by admixture with the isomeric colourless acetoxy-compound (XV) or with the acetoxy-derivative of 4-chloro-9-benzylanthracene (XVII) (Found : C, 76·4; H, 4·8. $C_{23}H_{17}O_2Cl$ requires C, 76·6; H, 4·7%).

(*b*) A solution of the colourless hydroxy-compound (XV; X = OH) (0·5 g.) in acetic acid (2 c.c.) and acetic anhydride (2 c.c.) was boiled for an hour, cooled, and diluted with alcohol. The yellow crystalline product melted at 157—158° alone or mixed with a sample of the acetoxy-compound prepared as described under (*a*).

This acetoxy-compound appeared to be readily hydrolysed by alcoholic potassium hydroxide, but the resulting hydroxy-compound could not be obtained crystalline on account of its excessive solubility.

Derivatives of 4-*Chloro*-9-*benzylanthracene.*

4-*Chloro*-9-*benzylanthracene*-ω-*pyridinium Bromide* (XVII; X = C_5H_5NBr).—A solution of the ω-bromo-compound (XVIII) in pyridine was heated on the water-bath for a few minutes and cooled and the solid in suspension was collected, washed with pyridine and with ether, dried, and recrystallised from alcohol–ether. The *salt* formed a yellowish crystalline powder, m. p. 220—225° (decomp.) after sintering and darkening at 215° (Found : Cl + Br, 25·2. $C_{26}H_{19}NClBr$ requires Cl + Br, 25·1%).

4-*Chloro*-ω-*hydroxy*-9-*benzylanthracene* (XVII; X = OH).—(*a*) The ω-bromo-compound (XVIII) was hydrolysed by heating with aqueous acetone in the presence of calcium carbonate in the same way as the isomeric 1-chloro-compound (p. 2807). The *hydroxy*-compound, thrice recrystallised from benzene–light petroleum, formed a yellowish crystalline powder, m. p. 98—100° (Found : C, 79·5; H, 5·1. $C_{21}H_{15}OCl$ requires C, 79·1; H, 4·7%).

(*b*) A solution of the ω-bromo-compound (XVIII; 3 g.) and sodium acetate (3 g.) in glacial acetic acid (25 c.c.) was boiled for ½ hour, and the cooled solution poured into water. The precipitated acetate, which could not be obtained crystalline, was hydrolysed with potassium hydroxide (5 g.) in alcoholic solution at the ordinary temperature. The product, twice recrystallised from benzene–light petroleum, melted at 98—100° alone or mixed with the hydroxy-compound prepared as described under (*a*). This second method of preparation suggests that the hydroxy-compound is the ω-hydroxy-compound, a hypothesis which is supported by the fluorescence and yellow colour of the substance and also by the

fact that it gave no red colour with boiling alcoholic potassium hydroxide solution (compare p. 2807). Methylation with methyl-alcoholic hydrochloric acid yielded the methoxy-compound described below.

4-*Chloro-ω-acetoxy-9-benzylanthracene* (XVII; X = O·COMe).—The hydroxy-compound described in the preceding paragraph was acetylated in the usual manner with pyridine–acetic anhydride at 100°, and after recrystallisation from benzene–light petroleum and from methyl alcohol the product formed pale yellow nodules, m. p. 129—130° (Found: C, 76·5; H, 4·8. $C_{23}H_{17}O_2Cl$ requires C, 76·6; H, 4·7%).

4-*Chloro-ω-methoxy-9-benzylanthracene* (XVII; X = OMe).—The ω-bromo-compound (XVIII; 3 g.) was heated on the water-bath for 1½ hours with methyl alcohol (100 c.c.) and calcium carbonate (2 g.). The product, recrystallised from methyl ethyl ketone–alcohol, formed pale yellow crystals, m. p. 144°, fluorescent in solution (Found: C, 79·2; H, 5·2. $C_{22}H_{17}OCl$ requires C, 79·2; H, 5·1%). This *methoxy*-compound was not changed when its solution in methyl alcohol containing hydrochloric or sulphuric acid was submitted to prolonged boiling.

A solution of the methoxy-compound (2·6 g.) in carbon disulphide (15 c.c.) was cooled in a freezing mixture and treated with bromine (0·4 c.c.). The additive compound was not isolated, the carbon disulphide being distilled off and the residue, which had a strong odour of benzaldehyde, treated with a little boiling alcohol. The resulting solid was recrystallised from acetic acid and from methyl ethyl ketone–alcohol and then formed straw-coloured needles; these melted at 152—153°, alone or mixed with the monobromo-derivative of α-chloroanthracene prepared by Barnett and Matthews (*Rec. trav. chim.*, 1924, **43**, 535), so that their compound must have structure (XIX) (Found: Cl + Br, 39·6. Calc.: Cl + Br, 39·6%).

4-*Chloro-ω-ethoxy-9-benzylanthracene* (XVII; X = OEt).—This was prepared from the bromo-compound (XVIII) by treatment with ethyl alcohol in the presence of calcium carbonate and formed yellowish nodules, m. p. 135—137°, from alcohol (Found: C, 79·5; H, 5·6. $C_{23}H_{19}OCl$ requires C, 79·7; H, 5·5%). This *ethoxy*-compound was fluorescent in solution and was not changed by heating with an alcoholic solution of hydrogen chloride.

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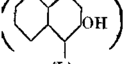
CCCLXXI.—*The Catalytic Production of Polynuclear Compounds. Part I.*

By George Roger Clemo and Robert Spence.

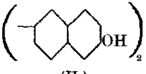
The chemistry of certain polynuclear compounds, some of which have assumed considerable commercial importance, *e.g.*, perylene, is but little known, and accordingly a study has been made in the first instance of certain compounds of intermediate complexity. The present communication deals with dinaphthylene oxides. The literature describes two of these compounds, one from α-naphthol (Merz and Weith, *Ber.*, 1881, **14**, 199), and the other obtained by Dianin (*Ber.*, 1875, **8**, 166) by dehydrating β-dinaphthol with phosphoric oxide. Eckstein (*Ber.*, 1905, **38**, 3660) has proved that compounds stated by Knecht and Unzeitig (*Ber.*, 1880, **13**, 1724) and by Walder (*Ber.*, 1882, **15**, 2166) to be isomeric with Dianin's compound are really identical with it. Further, Merz and Weith (*loc. cit.*) and Niederhausern (*Ber.*, 1882, **15**, 1122) claim to have produced from β-naphthol a specially pure form of Dianin's oxide, but it has now been found that, although the yield of this compound thus obtained is less than 5% of the theoretical, it is really isomeric with Dianin's compound (see p. 2812).

β-Dinaphthol (I) is easily obtained by oxidising β-naphthol with ferric chloride (Dianin, *J. Russ. Phys. Chem. Soc.*, 1874, **6**, 187), and the presence of the 1 : 1′-dinaphthyl linking in it was inferred by Julius (*Ber.*, 1886, **19**, 2549) from the fact that when it was distilled with zinc dust 1 : 1′-dinaphthyl appeared to be formed. Schoepfle, however (*J. Amer. Chem. Soc.*, 1923, **45**, 1566), has shown that a dinaphthylene oxide and not 1 : 1′-dinaphthyl results from this reaction.

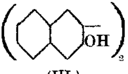
Hodgkinson and Limpach (J., 1891, **59**, 1100) distilled sodium 2-naphthol-6-sulphonate and, obtaining a mixture of β-naphthol, a dinaphthyl ether, and a dinaphthylene oxide, suggested that β-dinaphthol might have the constitution (II); whereas Pozzi Escot (*Compt. rend.*, 1904, **138**, 1618), from the fact that azo-derivatives of β-dinaphthol could be prepared, considered that the compound had the formula (III). It has been found, however, that



(I.)



(II.)

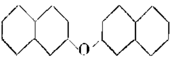


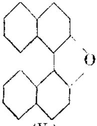
(III.)

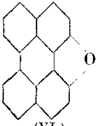
β-dinaphthol, together with a dinaphthylene oxide and a dinaphthylene dioxide (VII), is formed when 1-bromo-2-naphthol is

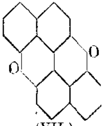
treated with copper powder, a result which indicates that (I) is its correct formula.

The dinaphthylene dioxide mentioned above has been prepared recently by Pummerer, Prell, and Rieche (*Ber.*, 1926, **59**, 2159) by heating the copper salt of β-dinaphthol at 280°, and in all probability it has the constitution (VII). The oxide produced by the dehydration of β-dinaphthol, therefore, will be 1 : 1′-dinaphthylene 2 : 2′-oxide (V), a conclusion borne out by its conversion into furoperylene (VI) by treatment with aluminium chloride (Weitzenbock, Seer, and von Bartsch, *Ber.*, 1913, **46**, 1994).


(IV.)


(V.)

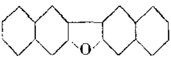

(VI.)


(VII.)

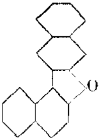
It has now been found that (I) can be converted into (V) by the agency of catalysts such as vanadium pentoxide, and further, that when β-naphthol itself is heated in an open-necked flask at 300° with the trioxide of either tungsten or molybdenum it is converted into the ether (IV); whereas if vanadium pentoxide be used, then, instead of (IV), β-dinaphthol is formed at 300°, and is converted into 1 : 1′-dinaphthylene 2 : 2′-oxide at 340°. If, however, in the latter experiment air is excluded from the flask, by fitting it with a long air condenser, or by the passage of a stream of carbon dioxide, then (IV) only is formed. In the above production of (V) from β-naphthol, therefore, the first reaction is the fairly rapid catalytic air-oxidation to (I), and is followed by catalytic dehydration to (V). All attempts to effect the catalytic air-oxidation of (IV) to (V) have failed. The *action of titanium dioxide is intermediate between* those of tungsten or molybdenum oxide and vanadium pentoxide, in that it gives a mixture of (IV) and (V) containing a considerable proportion of the former.

By the action of other catalysts, such as the alkaline-earth oxides, on β-naphthol an oxide isomeric with (V) is easily formed in quantity. This compound, hereinafter called the *isooxide*, is identical with that obtained in very small yield by Merz and Weith (*loc. cit.*). In this catalytic reaction a second compound, m. p. 300°, is formed, which corresponds to a compound mentioned by Niederhausern (*loc. cit.*), but insufficient has been obtained for investigation. The properties of the *iso*oxide point to its being a structural isomeride of (V) having the constitution (VIII) or (IX), and hence its formation appears to

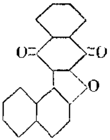
involve unusual reactivity of hydrogen in the β′-position in a mono-β-substituted naphthalene. The formation of 2-hydroxy-3-naph-



(VIII.)



(IX.)



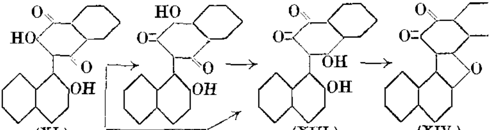
(X.)

thoic acid from sodium β-naphthoxide is the one well-established case of such β′-reactivity, and indicates that calcium β-naphthoxide also might be reactive in this position.

Both (V) and the *iso*oxide are stable to almost red-hot zinc dust and are scarcely acted on by fused potassium hydroxide. Reduction with hydriodic acid gives hydrogenated naphthalenes, and oxidation with sulphuric acid gives phthalic acid, in both cases. Chromic acid oxidation, however, destroys (V) but converts the *iso*oxide into a *quinone*, which does not condense with *o*-phenylenediamine and is therefore presumably of the para-type. Such marked difference in behaviour on oxidation suggests that the *iso*oxide is (IX) and not (VIII), for the latter would be expected to give a diquinone if a quinonoid compound were formed. The quinone is therefore probably (X).

When the quinone is distilled with zinc dust the *iso*oxide is regenerated, and on reduction with zinc and acetic anhydride it gives an O-*diacetyl* derivative which still contains the ether linking. The great stability of the furan ring of the *iso*oxide towards alkalis no longer persists in the quinone, however, for when this is treated with alcoholic sodium hydroxide the ring is easily opened to give a *dihydroxydinaphthaquinone*. This compound undergoes a remarkable change on heating: water is lost, but instead of the original *p*-quinone being regenerated an isomeric compound is produced. This forms red needles and condenses easily with *o*-phenylenediamine to give a substituted *phenazine*. It is therefore presumably an *o*-*quinone*. This transformation is explicable with formula (IX) for the *iso*oxide but not with (VIII): when the furan ring of the quinone (X) is opened, rotation of the top portion of the molecule seems to occur to give (XI), as evidenced by the formation, on treatment with acetic anhydride, of a yellow O-*diacetyl quinone* derivative. If rotation had not taken place, it would be expected that (X) would be re-formed under these conditions. The production of the *o*-quinone (XIV) from (XI), with the loss of water,

seems to necessitate the prior formation of (XIII). If this be grant the reaction appears to involve one or other of two contentic mechanisms, *viz.*, either the migration of a hydrogen atom from o oxygen atom to another in the meta-position with respect to the fir or the migration of the hydrogen in the first instance to an orth oxygen atom with temporary formation of the *m*-quinone (XI followed by a para-migration to give (XIII).

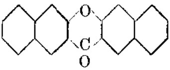


(XI.) (XII.) (XIII.) (XIV.)

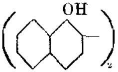
Whilst the above work was progressing an attempt was made synthesise the symmetrical 2 : 2′-dinaphthylene 3 : 3′-oxide (VII] The aim of the first series of experiments was to produce the 2 : 2′-c naphthyl linking and then to introduce the oxygen bridge. 2-Chlor 3-naphthoic acid was treated with copper powder as in the Ullmar reaction (Ullmann and Bielecki, *Ber.*, 1901, **34**, 2184), but onl β-naphthoic acid resulted; when ethyl 2-chloro-3-naphthoate wa used, the chlorine atom was found to be stable to copper-bronze i boiling nitrobenzene. A similar treatment of either 3-*brom* 2-*methoxynaphthalene* or its iodo-analogue gave only β-methox naphthalene, and 3-*bromo*-β-*naphthol* gave β-naphthol. Thes 2 : 3-disubstituted naphthalenes were prepared by applying th Hofmann reaction to 2-methoxy-3-naphthoamide. (Fries, *Ber* 1925, **58**, 2845, was unable to apply this reaction to 2-hydrox 3-naphthoamide, as it gave 1-bromo-2-hydroxy-3-naphthoamid instead of the amino-compound.) The second series of experiment aimed at the prior formation of the oxide linking and the subsequen introduction of the dinaphthyl link. The action of tungsten tri oxide and of vanadium pentoxide (see p. 2819) on 2-hydroxy-3-naph thoic acid and its ester was investigated with a view to preparin the dinaphthyl ether dicarboxylic acid. Then the Hofmann reactio on the di-amide, followed by diazotisation of the diamino-ethe and treatment with ammoniacal copper sulphate (Carpmael, E.I 278100, 1926), should give the oxide (VIII). Under all the con ditions tried, however, the condensation could not be stopped at th ether stage, but easily gave Strohbach's dinaphthaxanthone (XV (*Ber.*, 1901, **34**, 4144).

The action of catalysts on α-naphthol has also been investigated Vanadium pentoxide converts it into the α-dinaphthylene oxide o

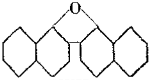
Merz and Weith (*loc. cit.*). The constitution of this compound follows from its preparation by the dehydration of α-dinaphthol. There was no direct evidence for the constitution of the latter compound until Willstätter and Schuler (*Ber.*, 1928, **61**, 362) showed that it is in all probability 1 : 1′-dihydroxy-2 : 2′-dinaphthyl (XVI).



(XV.)



(XVI.)



(XVII.)

Hence α-dinaphthylene oxide would appear to have the constitution (XVII). The same oxide results when α-naphthol is treated with calcium oxide, since, failing a Kaufler type of oxide as the result of a 4 : 4′-dinaphthyl linking, α-naphthol would be expected to form only one dinaphthylene oxide.

Experimental.

β-Dinaphthol (I).—1-Bromo-2-naphthol (22 g.), copper bronze (7·5 g.), and iodine (0·5 g.) were heated for 3 hours at 280°. The product was extracted with alkali, the filtered solution acidified with hydrochloric acid, and the precipitate collected and freed from β-naphthol by extraction with boiling water. The residue, crystallised from aqueous alcohol and from glacial acetic acid, gave needles, m. p. 216°, not depressed by admixture with a specimen of β-dinaphthol made by oxidising β-naphthol with ferric chloride (Found: C, 83·5; H, 5·1. Calc. for $C_{20}H_{14}O_2$: C, 83·9; H, 4·9%). From the alkali-insoluble material, boiling acetic acid extracted 1 : 1′-dinaphthylene 2 : 2′-oxide, which separated, on cooling, in needles, m. p. 156° (see below). The residue was crystallised from toluene and gave yellow needles (0·5 g.) of 1 : 1′-dinaphthylene 2 : 8′ : 2′ : 8-dioxide (VII), m. p. 236° (Found: C, 84·5; H, 3·5. Calc. for $C_{20}H_{10}O_2$: C, 85·1; H, 3·5%).

Catalytic Dehydration of β-Dinaphthol. 1 : 1′-Dinaphthylene 2 : 2′-Oxide (V).—β-Dinaphthol (25 g.) and vanadium pentoxide (1 g.) were gently boiled in a round-bottomed flask for 7 hours. When the product, which contained no alkali-soluble material, was vacuum-distilled, only almost pure 1 : 1′-dinaphthylene 2 : 2′-oxide (12 g.) passed over. This crystallised from benzene in pale yellow needles, m. p. 156° (Found: C, 89·5; H, 4·8. Calc. for $C_{20}H_{12}O$: C, 89·6; H, 4·5%). The oxide gives a purple colour in concentrated sulphuric acid, changing to red and then to dark brown on warming. The picrate has m. p. 164°.

Action of Catalysts on β-Naphthol.—(a) *Di-β-naphthyl ether* (IV). β-Naphthol (20 g.) and tungsten trioxide (0·5 g.) were heated in a

round-bottomed, long-necked flask (250 c.c.), first at 270° and then slowly to 300° as the β-naphthol reacted. After heating for 2 hours, the melt was poured into an excess of boiling caustic soda solution On cooling, the solid residue was collected (recovered β-naphthol, 3·3 g.), dried (14 g.), and vacuum-distilled. The total distillate (12·5 g.) was crystallised from ligroin and gave colourless plates, m. p. 105°.

(b) β-*Dinaphthol.* β-Naphthol (20 g.) and vanadium pentoxide (0·5 g.) were heated as in (a), for 5 hours, at 300°. The product was extracted with boiling sodium hydroxide solution, in which it was almost completely soluble, and the hot filtered solution was treated with excess of hydrochloric acid. After cooling, the precipitate was collected and extracted with boiling water to remove unchanged β-naphthol. The residual β-dinaphthol (8 g.), after crystallising from glacial acetic acid, had m. p. 216°.

(c) 1 : 1′-*Dinaphthylene* 2 : 2′-*oxide* (V). β-Naphthol (100 g.) and vanadium pentoxide (1 g.) were heated in a flask for 5 hours, the temperature rising slowly from 270° to 340°. The product was extracted with alkali, and β-naphthol (4 g.) and crude β-dinaphthol (13 g.) were obtained from the extract. The dark alkali-insoluble residue was dried (50 g.) and distilled, giving 43 g. of a pale yellow solid which, when crystallised from benzene–alcohol to free it from a little di-β-naphthyl ether, gave 1 : 1′-dinaphthylene 2 : 2′-oxide (30 g.), m. p. 156°.

(d) iso*Dinaphthylene oxide* (IX). β-Naphthol (100 g.) and calcium oxide (1 g.) were heated as in (c) for 10 hours, the temperature being raised slowly from 270° to 340°. The product was treated with alkali to free it from unchanged β-naphthol, and the residue distilled. The distillate, a colourless solid (44 g.), was extracted with benzene (300 c.c.), leaving 0·5 g. of the solid of m. p. 300° (see p. 2812). Alcohol (300 c.c.) was added to the extract; the colourless plates of the iso*oxide* (30 g.) thus obtained, after recrystallisation from glacial acetic acid, melted at 158—159°; mixed m. p. with (V), 130—140° (Found : C, 89·3; H, 4·4. $C_{20}H_{12}O$ requires C, 89·6 H, 4·5%). The compound is easily soluble in benzene, less soluble in alcohol, and gives in sulphuric acid an orange-red solution, which changes through scarlet, purple, and blue to light brown on warming

*Dibromo*iso*dinaphthylene Oxide.*—When the *iso*oxide (3·6 g.) dissolved in carbon disulphide, was slowly treated with bromine (2·5 c.c.), colourless needles of the *dibromo*-compound separated (5·9 g.), which, after recrystallisation from benzene and from acetic acid, had m. p. 193° (Found: Br, 37·4. $C_{20}H_{10}OBr_2$ requires Br, 37·6%).

Oxidation of 1 : 1′-*Dinaphthylene* 2 : 2′-*Oxide* (V) *and of the* iso

)xide.—(a) *With sulphuric acid.* Concentrated sulphuric acid 50 c.c.) and either of the above two oxides (7 g.), with a little nercury and copper sulphate as catalyst, were heated together. On listillation, phthalic acid (1·3 g.) (anhydride, m. p. 128°) passed over.

(b) *With chromic acid.* iso*Dinaphthaquinone oxide* (X). The *so*oxide (10 g.) was refluxed for 10 minutes with 250 c.c. of a chromic ıcid mixture (made by dissolving potassium dichromate, 60 g., in concentrated sulphuric acid, 80 g., and water, 270 c.c.), water was hen added, and the solid collected. It was crystallised first from ıcetic acid (solubility, 0·5%) and then from pyridine, bronze leaflets 4·5 g.) being obtained, m. p. 268° (Found: C, 80·2; H, 3·5. $C_{20}H_{10}O_3$ requires C, 80·5; H, 3·4%). The *quinone* sublimes ınchanged, and gives in sulphuric acid a bluish-green solution which becomes brown on heating.

After 1 : 1′-dinaphthylene 2 : 2′-oxide has been treated with chromic acid as above, no solid is obtained on dilution with water.

Reduction of the Quinone (X). *Diacetoxy*iso*dinaphthylene Oxide.*—The quinone (5 g.) and acetic anhydride (20 c.c.) were refluxed for 15 minutes in presence of zinc dust (5 g.). The liquid was filtered and poured into water with rapid stirring. The colourless solid obtained crystallised from acetic acid in needles (5 g.), m. p. 245—246° Found: C, 75·0; H, 4·0. $C_{24}H_{16}O_5$ requires C, 75·0; H, 4·2%).

Hydrolysis of the Quinone.—The quinone (4 g.) was refluxed with alcoholic sodium hydroxide (1 l. of 0·5% solution) for 10 hours and the solution was then concentrated to small bulk, diluted with water, and filtered. The filtrate, treated with an excess of hydrochloric acid, gave a reddish-brown precipitate, which was washed with water and dried in a vacuum desiccator (3·8 g.). It crystallised from chloroform in light red prisms with solvent of crystallisation, which was driven off by heating on the water-bath; m. p. 222° (Found: C, 76·0; H, 3·5. $C_{20}H_{12}O_4$ requires C, 75·9; H, 3·8%). *Dihydroxydinaphthaquinone* crystallises from benzene in needles, with benzene of crystallisation, and from acetic acid in rhombohedra.

Diacetoxydinaphthaquinone.—Dihydroxydinaphthaquinone (0·5 g.) was refluxed with acetic anhydride (20 c.c.) and a drop of pyridine for 10 minutes, and the mixture poured into water. The precipitate obtained was crystallised first from glacial acetic acid and then twice from alcohol, giving golden-yellow needles, m. p. 167° (Found: C, 71·7; H, 4·3. $C_{24}H_{16}O_6$ requires C, 72·0; H, 4·0%). This *diacetyl* compound gives a reddish-brown colour with concentrated sulphuric acid, and dissolves in hot potassium hydroxide solution with a red colour, the original dihydroxydinaphthaquinone being precipitated by the addition of hydrochloric acid.

o-*Dinaphthaquinone Oxide* (XIV).—The dihydroxy-quinone (2 g.)

was heated at 250°, and after about 5 minutes evolution of ste ceased. The product crystallised from benzene in deep red need (1·1 g.), m. p. 255—256° (Found: C, 80·7; H, 3·4. $C_{20}H_{1}$ requires C, 80·5; H, 3·4%). The *o-quinone oxide* gives with s phuric acid a brown colour which turns green on warming.

Condensation to a phenazine. The *o*-quinone oxide (0·3 g.) a *o*-phenylenediamine (0·2 g.) were refluxed in acetic acid (60 c for ½ hour. After cooling, the solid was collected; it crystalli from glacial acetic acid in yellow needles (0·25 g.), m. p. 240° (Foun N, 7·3. $C_{26}H_{14}ON_2$ requires N, 7·6%).

Action of Copper-bronze on 2-Chloro-3-naphthoic Acid.—2-Chlo 3-naphthoic acid (10 g.) was dissolved in nitrobenzene (50 c. copper-bronze (25 g.) added, and the mixture refluxed for 2 hou A solution of sodium hydroxide was then added, the nitrobenze removed in steam, and the residual alkaline solution filtered a acidified. The resulting precipitate crystallised from acetone needles (4 g.), m. p. 185°, and gave an amide, m. p. 197°, and w therefore β-naphthoic acid.

2-*Methoxy-3-naphthoic Acid.*—2-Hydroxy-3-naphthoic acid (10 g treated with methyl sulphate and sodium hydroxide, gave 11 g. 2-methoxy-3-naphthoic acid. This was converted into the ami m. p. 170° after crystallising from acetone.

2-*Methoxy-3-naphthylamine.*—Chlorine, from potassium perma anate (5·3 g.), was passed into an ice-cooled solution of sodium hy oxide (14 g.) in water (100 c.c.). The resulting hypochlorite w added to the finely powdered amide (15 g.) and warmed in a wat bath with stirring, the temperature being kept below 70° until reaction had subsided. Sodium hydroxide solution was then add the mixture heated on a water-bath for an hour, the amine extrac with benzene, the benzene removed, and the residue distilled un reduced pressure. The distillate crystallised from methyl alcohol colourless plates (5 g.), m. p. 109·5° (Found: C, 76·1; H, 6 N, 8·4. $C_{11}H_{11}ON$ requires C, 76·3; H, 6·4; N, 8·1%). T *amine* forms an *acetyl* derivative which crystallises from meth alcohol in colourless plates, m. p. 124—125° (Found: C, 73 H, 6·2. $C_{13}H_{13}O_2N$ requires C, 72·6; H, 6·1%).

3-*Bromo-2-methoxynaphthalene.*—2-Methoxy-3-naphthylami (17 g.), in a mixture of concentrated hydrochloric acid (20 c.c.) a water (150 c.c.), was diazotised with sodium nitrite (7 g.). solution of cuprous bromide (prepared from copper sulphate, 20 in hydrobromic acid (30 c.c.; *d* 1·44) was cooled in ice, and t diazo-solution added. After ½ hour, the mixture was warmed on t water-bath until no more nitrogen was evolved; the product w then extracted with benzene, and the extract fractionated. T

raction of b. p. 178—190°/16 mm. (6·5 g.) was crystallised from uethyl alcohol and then from ligroin (b. p. 40—60°), giving colourless lates, m. p. 76° (Found : Br, 33·2. $C_{11}H_9OBr$ requires Br, 33·75%).

3-Iodo-2-methoxynaphthalene.—2-Methoxy-3-naphthylamine (5 g.) ras diazotised as above, and an aqueous solution of potassium odide (5 g.) added. The solution was stirred for ½ hour, heated to oiling, made alkaline, and extracted with benzene. The benzene ras removed, and the residue vacuum-distilled, giving a pale yellow il which solidified; it crystallised from methyl alcohol in colourless risms, m. p. 65° (Found : I, 44·2. $C_{11}H_9OI$ requires I, 44·7%).

3-Bromo-β-naphthol. — 3-Bromo-2-methoxynaphthalene (4·5 g.) ras refluxed with hydrobromic acid (50 c.c.; *d* 1·44) for 4 hours, and he mixture was then diluted with water and cooled, and the solid ollected. This was extracted with sodium hydroxide, the filtered olution acidified, and 3-*bromo*-β-*naphthol* dried and distilled (2 g.). t crystallised from ligroin (b. p. 40—60°) in well-defined needles, ı. p. 80—81°; mixed m. p. with 1-bromo-β-naphthol (m. p. 84°), 5—55°. As the bromine determinations were always about 1% low, he product probably contained a small amount of β-naphthol Found : Br, 34·7. $C_{10}H_7OBr$ requires Br, 35·9%).

The use of hydriodic acid instead of hydrobromic acid for demethyl-tion resulted in both 3-bromo- and 3-iodo-2-methoxynaphthalene eing reduced to β-naphthol.

Dinaphthaxanthone.—2-Hydroxy-3-naphthoic acid (6 g.) and ıngsten trioxide (0·05 g.) or vanadium pentoxide were heated ogether for ½ hour, the residue was extracted with alkali, and the ısoluble portion was dried and distilled under reduced pressure. he distillate (2 g.) crystallised from glacial acetic acid in long, ellow needles, m. p. 134—135° (Found : C, 85·3; H, 4·1. Calc. for $_{21}H_{12}O_2$: C, 85·1; H, 4·1%). Ethyl 2-hydroxy-3-naphthoate ıve the same result.

2 : 2′-*Dinaphthylene* 1 : 1′-*Oxide* (XVII).—α-Naphthol (20 g.) was eated with vanadium pentoxide (1 g.) for 4 hours, the temperature sing to 340°. The product was extracted with alkali, and the soluble portion distilled. The distillate crystallised from benzene-cohol in yellow needles, m. p. 179° (Found : C, 89·2; H, 4·6. alc. for $C_{20}H_{12}O$: C, 89·6; H, 4·5%).

One of the authors (R. S.) wishes to thank the Department of cientific and Industrial Research for a grant which has enabled m to take part in this investigation.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE. [Received, August 2nd, 1928.]

CCCLXXII.—*The Crystal Structure of Silver Subfluoride.*

By HENRY TERREY and HUGH DIAMOND.

THE peculiar valency relationships existing in sub-compounds make it desirable to establish conclusively the existence of these substances as definite chemical individuals, and for this purpose *X*-ray methods appear to yield the most promising results (compare Levi, *Gazzetta*, 1924, **54**, 598). Silver subfluoride, Ag_2F, one of the most interesting and well-defined of these compounds, was chosen for investigation in this manner, but a specimen of the substance prepared by Wöhler's method (*Z. anorg. Chem.*, 1912, **78**, 242) yielded unsatisfactory *X*-ray photographs in which the presence of silver lines indicated the heterogeneity of the sample. However, since the commencement of this work, Hettich (*ibid.*, 1927, **167**, 70) has prepared large crystals of silver subfluoride electrolytically and demonstrated its chemical entity by an *X*-ray comparison of his product with silver and with the normal fluoride. Hettich's method of preparation was therefore adopted by us, and our main object was then confined to the elucidation of the crystal structure of silver subfluoride as revealed by its *X*-ray diffraction pattern.

Silver subfluoride crystals, prepared by electrolysing a concentrated solution of silver fluoride at 60° with a low current density were washed with alcohol and ether and dried in a vacuum (Found total Ag, 91·5; soluble Ag, 45·1; F, 8·0. Calc.: total Ag, 91·9 soluble Ag, 45·95; F, 8·1%).

A comparison photograph of silver subfluoride and sodium chloride was obtained by the powder method of Debye–Scherrer and Hull, a Shearer tube fitted with a copper anticathode being used as a source of *X*-radiation. The results of measurements made upon this photograph are given in Table I, the calculated values of d_{hkil}/n being based on a hexagonal lattice of side 2·98 Å.U. and height 5·710 Å.U., which was deduced from the observed values of the interplanar spacings by means of Hull's plots (*Physical Rev.*, 1921, **17**, 549). One molecule of Ag_2F in a cell of these dimensions requires a density of 8·78, whereas the experimentally determined value is 8·64 (Hettich gives 8·57).

In Table II are recorded measurements made upon a plain silver subfluoride photograph, and the strong lines have been employed for calibration purposes, data from Table I being used. In this way it has been possible to identify the weak lines and thus obtain useful information for intensity considerations.

TABLE I.

Sodium chloride.			Silver subfluoride.						
d_{hkil} of standard lines.	Distance between corresponding lines.	Calculated value of camera radius.	Distance between corresponding lines.	Estimated value of camera radius.	Angle of reflexion, θ.	Cosec θ.	d_{hkil}/n obs.	d_{hkil}/n calc.	Indices, $hkil$.
			15·575	3·001	15° 38′	3·711	2·857	2·855	0002
2·814	15·525	3·001							
			14·850	3·000	19 5	3·059	2·355	2·358	1011
1·990	14·075	2·999							
			13·850	2·999	23 41	2·490	1·917	1·918	1012
								1·903	0003
1·625	12·925	3·000							
			12·550	2·999	29 46	2·014	1·551	1·533	1013
			12·350	2·998	30 59	1·943	1·496	1·495	1120
1·407	11·887	2·997							
1·258	10·975	3·010		which coincides with				1·250	1014
			10·275	3·007	41 2	1·523	1·173	1·179	2022
								1·175	1123
1·149	10·050	3·005							
			8·875	3·009	46 54	1·370	1·054	1·045	1015
								1·032	1124
0·938	7·325	3·013							
			6·725	3·011	58 1	1·179	0·908	0·908	1125
0·890	6·325	3·010		which coincides with				0·893	1016
								0·885	2132

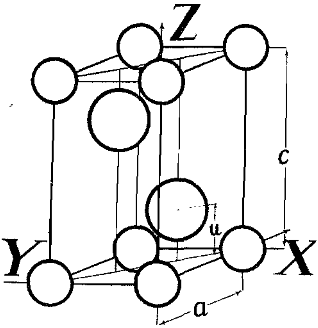
TABLE II.

d_{hkil} of standard lines.	Distance between corresponding lines.	Calculated value of camera radius.	Distance between corresponding lines.	Estimated value of camera radius.	Angle of reflexion, θ.	Cosec θ.	d_{hkil}/n obs.	d_{hkil}/n calc.	Indices, $hkil$.
2·855	15·540	2·994							0002
			15·220	2·993	17° 16′	3·369	2·594	2·590	1010
2·358	14·820	2·992							1011
			13·850	2·991	23 40	2·491	1·918	1·918	1012
1·903	13·810	2·991							0003
			12·470	2·987	30 11	1·989	1·531	1·533	1013
			12·350	2·986	30 45	1·956	1·505	1·495	1120
			11·377	2·985	35 24	1·726	1·329	1·325	1122
			10·955	2·984	37 25	1·646	1·267	1·262	2021
1·250	10·830	2·984							1014
1·175	10·270	2·989							1123
									2022
			9·912	2·989	42 30	1·480	1·140	1·144	0005
			8·625	2·989	48 40	1·332	1·025	1·045	1015
								1·032	1124
			7·775	2·990	52 45	1·256	0·967	0·978	2130
								0·964	2131
0·908	6·675	2·990							1125
			6·305	2·990	59 47	1·157	0·891	0·893	1016
								0·885	2132

Silver subfluoride is a hard, metallic-looking substance, not easily reduced to powder in a mortar. It seems probable, therefore, that the atoms of silver and fluorine are closely packed, and the compound would appear to have a "cadmium iodide" structure.

This is shown in Fig. 1, in which the large circles denote silve atoms and the small circles fluorine atoms. Fluorine occupies th position (0, 0, 0) and silver the positions ($\frac{1}{3}$, $\frac{2}{3}$, μ) and ($\frac{2}{3}$, $\frac{1}{3}$, $\bar{\mu}$). Th value of the parameter μ, the distance between successive planes c silver and fluorine atoms, may be deduced from intensity cor siderations, and for this purpose the relations between the inter sities of the various orders of reflexion from the 0001 plane ar valuable. It has been possible to obtain crystals with well developed faces parallel to the 0001 plane and also to the 101 plane, and to record the various orders of reflexion from then The observed intensities of the first-, second-, and third-orde reflexions from the 000 plane do not exhibit normal decline : th second order is stronge than the first, and th third order is stronge than the first bu weaker than the second A weak fifth-order re flexion also occurs. I the case of the 101 plane only a first-orde reflexion is obtained In Table III an esti mated value of th intensity of reflexion i given for each line ob served, and intensitie calculated for severa values of μ are also given for comparison. The lines have bee divided into groups in which each is derived from the same typ of plane. Some of the lines are unresolved doublets, and in thes cases it has been impossible to assign any definite observed intensit values to the components. The indices of co-operating planes hav therefore been inserted after the observed intensity value.

FIG. 1.



The expression $I = NS^2/\sin^2\theta$, where N is the number of co-operating planes and $S = 10 + 46[e^{i2\pi n(h/3 + 2k/3 + \mu l)} + e^{i2\pi n(2h/3 + k/3 + \bar{\mu} l)}]$ has been used in the above calculations.

The most satisfactory agreement between observed and calculatec values occurs when $\mu = 0{\cdot}3$. There is, however, an obvious dis crepancy in the case of the 1120 plane, but this could not b eliminated by a change of μ. Apart from this inconsistency, th general similarity of observed and calculated intensities in eacl

TABLE III.

Indices of plane *hkil*.	Observed intensity.	Intensity calculated for different values of μ. 0·1.	0·2.	0·3.	0·4.	0·5.
0001	7	385	77	17	217	356
0002	10	20	56	56	20	143
0003	*9*	*5*	*25*	*43*	*9*	*41*
0004	—	14	5	5	14	35
0005	2 (1124)	15	22	15	22	15
0006	—	6	2	2	6	16
1010	2	110	110	110	110	110
2020	—	11	11	11	11	11
1011	9	300	360	216	0	222
1012	8	240	0	321	198	43
1013	*3*	*66*	*172*	*11*	*150*	*68*
1014	7	0	84	102	138	18
1015	1	32	12	32	12	32
1016	7 (2132)	68	50	43	12	10
1120	1	240	240	240	240	240
1121	—	137	28	6	78	131
1122	2	25	73	73	24	187
1123	5 (2022)	4	58	99	14	95
1124	*2 (0005)*	*43*	*15*	*15*	*43*	*110*
1125	7	56	87	56	87	56
2021	1	154	81	218	218	53
2022	5 (1123)	71	124	0	90	19
2130	2 (2131)	30	30	30	30	30
2131	*2 (2130)*	*51*	*34*	*25*	*0*	*13*
2132	7 (1016)	51	0	71	42	9

group is good, and it is suggested that a "cadmium iodide" structure, with μ = app. 0·3, is fairly representative of silver subfluoride.

When $\mu = 0{\cdot}3$, the atomic diameter of silver with respect to silver is about 2·8 Å.U. and with respect to fluorine about 3·6 Å.U., and it is significant that these values are equal to the atomic diameters of silver in the metallic state and in normal combination, respectively. This seems to indicate that the relation between adjacent silver atoms resembles that existing in the metallic state, and that the relation between adjacent silver and fluorine atoms is similar to that in normal silver fluoride. Perhaps in the formation of a molecule of subfluoride two silver atoms partly share their uncompleted rings of electrons, leaving between them in reserve an electron to complete the electron ring of a fluorine atom. If this be the case, previous hypotheses postulating the existence of "sub-ions" would appear to have some justification, and the metallic properties of silver subfluoride (*e.g.*, electrical conductivity of the order of that of graphite) would find a ready explanation.

Summary.

Silver subfluoride has been examined by the powder method, and found to possess a hexagonal unit cell of dimensions $a = 2{\cdot}989$ Å.U. and $c = 5{\cdot}710$ Å.U. The density corresponds to one molecule in the unit cell. *Intensity considerations appear to agree with a*

" cadmium iodide " structure with the parameter μ equal to about 0·3.

In conclusion, one of us (H. D.) wishes to express his grateful thanks to the Salters' Institute for a grant which has enabled him to take part in this research.

THE SIR WILLIAM RAMSAY LABORATORIES OF INORGANIC AND PHYSICAL CHEMISTRY, UNIVERSITY COLLEGE, LONDON. [Received, June 29th, 1928.]

NOTES.

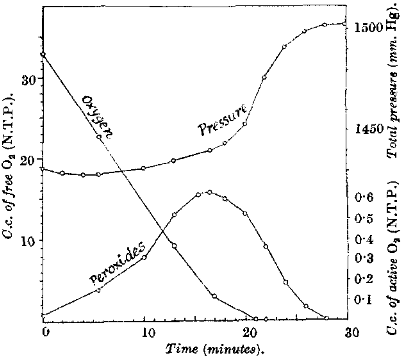
The Oxidation of n-*Hexane.* By MAX BRUNNER and ERIC KEIGHTLEY RIDEAL.

IN a previous communication (this vol., p. 1162), it was shown that *n*-hexane–air mixtures in a closed bulb maintained at temperatures well below the so-called critical inflexion temperature or temperature of initial combustion actually underwent reaction at appreciable velocities. The pressure–time curves all exhibited well-marked characteristics, a period of no or small pressure change followed by a short and final period of rapidly rising pressure. It was assumed that these two periods were characterised in their rates of reaction, it being thought that the " induction " period was a period of slow combustion, which was followed by a period of rapid combustion, this being initiated by a rising content of peroxide molecules. Further investigation on the rate of oxygen consumption, whilst confirming the view that the period of rapid pressure increase is associated with an oxidation process by means of peroxide molecules formed prior to the observed pressure increase, has shown that the rate of oxygen uptake during the initial period of no pressure change, previously called the induction period, is in reality quite rapid. This is made clear from a consideration of the curves representing the analyses, conducted as previously described, after various periods of time of a 42% (by volume) hexane–58% oxygen mixture maintained in a bulb of 57·9 c.c. capacity at 210°. It is evident that the rapid increase in pressure occurs when the oxygen has almost disappeared and is to be attributed to reactions involving decomposition or reaction of peroxide molecules. It is significant that the rate of oxygen uptake appears to be a zero-order reaction over a wide range of pressure.

The results of a detailed examination of the varied compositions of the reaction products during this period of isopiestic combustion have been described by one of us (M. B., *Helv. Chim. Acta*, Oct.,

1928), but it is clear that observations on the rate of change of pressure or volume or on the content of substances giving peroxide reactions, two methods frequently adopted, are not safe criteria for determination of reaction velocities in the slow combustion of hydrocarbons. The reactions which appear to predominate in the

FIG. 1.



initial stages of combustion in glass vessels at low temperatures may be summarised by the equations

$$C_6H_{14} + O_2 \longrightarrow C_6H_{14}O_2 \text{ (active moloxide)}$$
$$C_6H_{14} + C_6H_{14}O_2 \longrightarrow 2C_6H_{12} + 2H_2O$$
$$C_6H_{12} + O_2 \longrightarrow C_6H_{12}O_2 \longrightarrow \text{decomposition.}$$

Although, at low temperatures, surfaces appear to play an important part in the formation of peroxides, consideration of the great reaction velocity during the period of no pressure change leads us to suspect that the peroxides themselves cannot be the reaction centres for the propagation of the chemical action through the homogeneous bulk phase.—THE UNIVERSITIES OF ZÜRICH AND CAMBRIDGE. [*Received, August 10th*, 1928.]

The Preparation of Cholestenone. By WILFRED ARCHIBALD SEXTON.

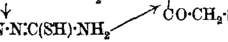
A MIXTURE of pure cholesterol (20 g.) and copper bronze (15 g.) was heated gently at 2—3 mm. pressure in a 200 c.c. Jena glass distillation flask (see Heilbron and Sexton, this vol., p. 347). As soon as

the sterol was molten a violent reaction commenced with evolution of a thick white vapour. This condensed as a white powder in a second distillation flask serving as receiver; glass wool in a U-tube placed between the side arm and the pump effectually prevented the escape of solid particles. After a few minutes the violence of the reaction abated and the catalyst became caked together in a porous mass. The sublimate (0·2 g.) proved to be unchanged cholesterol. The temperature was then gradually raised until distillation commenced. The distillate (280—290°/3—4 mm.) (17 g.) was golden-yellow and of high viscosity. It crystallised from methyl alcohol at 0° in white needles (6 g.), m. p. 72—76°, which was raised to 80° by repeated crystallisation from methyl alcohol: no depression of m. p. occurred on heating a mixture with cholestenone prepared by heating the sterol with copper oxide. It gave the characteristic semicarbazone, m. p. 234°. By evaporation of the filtrate in a desiccator over calcium chloride a further crop (10 g.) of crude cholestenone was obtained (total yield, 80%).—THE UNIVERSITY, LIVERPOOL. [*Received, August 25th*, 1928.]

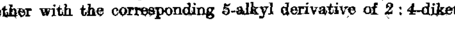
The so-called Bisthiohydantoins of Frerichs, Förster, and Höller.
By HERBERT WILLIAM STEPHEN and FORSYTH JAMES WILSON.

BY the interaction of hydrazodithiodicarbonamide and chloroacetic acid in boiling aqueous solution, Frerichs and Förster (*Annalen*, 1909, **371**, 257) obtained a compound which they regarded as 3 : 3-bisthiohydantoin (or, according to present nomenclature, 3 : 3-bis-ψ-thiohydantoin); and in a similar manner, from α-bromo-propionic and -*n*-butyric acids Frerichs and Höller (*ibid.*, 1913, **398**, 256) obtained compounds considered to be substituted 3 : 3-bis-ψ-thiohydantoins (R = Me or Et):

$NH_2{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH_2 + 2CHRBr{\cdot}CO_2H =$


$+ 2H_2O + 2HBr.$

In a recent communication (this vol., p. 1415) we showed from the products of hydrolysis that the so-called 3 : 3-bis-ψ-thiohydantoin is really 2 : 4-diketotetrahydrothiazole-2-ketazine (I), and its formation would therefore be represented thus:


(I).

We have now shown that the two compounds described by Frerichs and Höller give on hydrolysis hydrazine hydrochloride together with the corresponding 5-alkyl derivative of 2 : 4-diketo-

tetrahydrothiazole; and we therefore regard these compounds as 2 : 4-diketo-5-alkyltetrahydrothiazole-2-ketazines.

Frerichs and Höller, in noting that the alleged 3 : 3-bis-ψ-thiohydantoins are more acidic than basic, remark that this is somewhat surprising, since ψ-thiohydantoin is more basic than acidic; but the acidity of these compounds is to be expected from the structures now assigned, since the 2 : 4-diketotetrahydrotbiazoles are acidic.

2 : 4-*Diketo-5-methyltetrahydrothiazole-2-ketazine*, prepared hy the method of Frerichs and Höller from hydrazodithiodicarbonamide and α-bromopropionic acid, melted sharply at 289° and possessed the properties ascribed to it by these authors, who give the m. p. as above 280°. It was boiled for ½ hour with concentrated hydrochloric acid, and the solution evaporated on the water-bath and finally in a vacuum over soda–lime and concentrated sulphuric acid. Extraction with hot benzene left a residue of bydrazine hydrochloride (identified by conversion into benzalazine), and the extract on evaporation left a viscous oil which solidified after distillation (166—168°/20 mm.); the solid was crystallised from benzene–light petroleum and then had m. p. 46—47°. From its properties this was evidently 2 : 4-diketo-5-methyltetrahydrothiazole (Wheeler and Barnes, *Amer. Chem. J.*, 1900, **24**, 60; Wilson and Burns, J., 1923, **123**, 799).

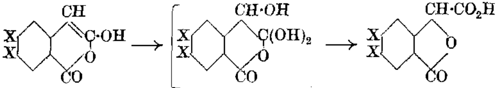
2 : 4-*Diketo-5-ethyltetrahydrothiazole-2-ketazine*, similarly prepared from α-bromo-*n*-butyric acid, crystallised from glacial acetic acid in slightly rose-coloured plates and, when freed from solvent of crystallisation by washing with ether, had m. p. 233° (Frerichs and Förster give 225—226°) (Found: N, 19·6. Calc.: N, 19·6%). Hydrolysis as in the preceding case yielded hydrazine hydrochloride, and evaporation of the benzene extract left a colourless oil which solidified on cooling; crystallisation of the solid from benzene–light petroleum gave prisms, m. p. 64—65°, identical with 2 : 4-diketo-5-ethyltetrahydrothiazole (Wheeler and Barnes; Wilson and Burns, *locc. cit.*).

We wish to thank the Governors of this College for a Research Assistantship awarded to one of us (H. W. S.).—THE ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, July 26th,* 1928.]

The Enolisation of Homophthalic Anhydrides. By THOMAS STEVENS STEVENS and JAMES LEGGAT WILSON.

4 : 5-*Methylenedioxyhomophthalic anhydride* (enolic form as I, XX = CH_2O_2) not only resembles the unsubstituted homophthalic anhydride in forming yellow alkali salts (compare Dieckmann,

Ber., 1914, **47**, 1428), but is itself deep yellow in the solid state, unlike homophthalic anhydride on the one hand and methylenedioxyhomophthalic acid on the other. A general investigation of the behaviour of analogous substances was planned, but as a paper bearing on this subject has recently appeared (Davies and Poole, this vol., p. 1616), it was deemed advisable to publish the results so far obtained.



(I.) (II.)

4 : 5-Methylenedioxyhomophthalic anhydride is obtained by boiling the parent acid with excess of acetyl chloride for several hours, until the original white powder has been replaced by yellow crystals. It separates from benzene in yellow needles, m. p. 178—180° [Found : equiv. in ice-cold acetone, 199·8; in boiling water, 102·1. $C_{10}H_6O_5$ requires equiv. 206 (monobasic), 103 (dibasic)]. The anhydride is not readily affected by bromine, but gives a dark brown precipitate with ferric chloride under the conditions specified by Davies and Poole (*loc. cit.*) for homophthalic anhydride.

Preliminary experiments on the methylation of homophthalic anhydride led to no definite result. An estimation by Hieber's method (*Ber.*, 1921, **54**, 902) indicated a small percentage of enol, but no great reliance is to be placed on the observation, as the formation of a stable chelate ring-system (on which the whole method presumably depends) is improbable in the present case. On the other hand, Dieckmann's general criticism (*Ber.*, 1921, **54**, 2251) of the Hieber reaction may not apply here, as the anhydride is a well-defined acid.

When the calculated amount of aqueous permanganate was added to an ice-cold alkaline solution of homophthalic anhydride, phthalidecarboxylic acid (II, X = H), m. p. 151°, was produced, which gave phthalide, m. p. 73°, on heating. Methylenedioxyhomophthalic anhydride similarly yielded methylenedioxyphthalide-*carboxylic acid*, m. p. 213—215° (decomp.) (Ruhemann, J., 1912, **101**, 783, gives 216° decomp.), and methylenedioxyphthalide, m. p. and mixed m. p. 188—189° (Stevens and Robertson, J., 1927, 2790).—The University, Glasgow. [*Received, September* 21*st*, 1928.]

Preparation of 4-Bromophthalic Acid. By LESLIE CHARLES BAKER.

PHTHALIC anhydride was converted into ethyl 4-nitrophthalate by Miller's method (*Annalen*, 1881, **208**, 224; compare also Cohen, Woodroffe, and Anderson, J., 1916, **109**, 226), and this compound reduced to the amino-ester by Baeyer's method (*Ber.*, 1877, **10**, 1079). (This reduction is best effected at 30—40°, since at lower temperatures the ester tends to solidify when liberated from its alcoholic solution by the addition of acid.) From the precipitate obtained by neutralising the solution with sodium carbonate, after drying, hot absolute alcohol extracted ethyl 4-aminophthalate in 71% yield. This ester (12 g.) was diazotised at 0° (concentrated hydrochloric acid 36 c.c., water 95 c.c.; sodium nitrite 8 g.), and the resulting mixture poured into an ice-cold solution of cuprous bromide (8 g.) in hydrobromic acid (20 c.c.); after ½ hour, the whole was boiled. An ethereal extract of the cold solution, after being washed with dilute acid, sodium carbonate, and water and dried, yielded 10 g. of ethyl 4-bromophthalate (66%) as a pale yellow oil, b. p. 194—195°/16 mm. Von Braun (*Ber.*, 1923, **56**, 2332) gives the b. p. as 190—191°/16 mm.

A mixture of ethyl 4-bromophthalate (7 g.) and baryta (9 g.) in water (140 c.c.) and alcohol (100 c.c.) was heated for 2—3 hours with shaking, the solution was then acidified with concentrated hydrochloric acid, and the alcohol boiled off. Hot *N*-sulphuric acid (65 c.c.) was added slowly with stirring, the precipitated barium sulphate removed when cold, and the filtrate concentrated; 4-bromophthalic acid (5 g.; 88% yield) then separated, m. p. 173—175° after recrystallisation from water.—UNIVERSITY COLLEGE, LONDON. [*Received, October 1st*, 1928.]

CCCLXXIII.—*The Photochemical Decomposition of Glyoxal.*

By RONALD G. W. NORRISH and JOHN G. A. GRIFFITHS.

GLYOXAL in its monomeric form is a volatile yellow liquid (b. p. 50°) and constitutes the simplest of organic coloured compounds. It has been found possible to keep the dry gas in a tube for several hours without rapid polymerisation. Its photochemistry does not appear to have been studied, although its absorption spectrum in the gaseous state has been measured by Purvis and McCleland (J., 1912, **101**, 1810) and by Luthy (*Z. physikal. Chem.*, 1923, **107**, 302). The last author found a very large number of narrow absorption bands stretching from the blue at 4548 Å.U. to the ultra-

violet at *ca.* 3000 Å.U., but measurement of fine structure became difficult after λ 3400 Å.U. on account of the weakness of absorption. The results of Purvis and McCleland are in geueral agreement with these observations. The strongest absorption occurs in the blue-violet region for a group of bands lying between 4554 and 4123 Å.U., those lying beyond this region being much weaker and only measurable at higher pressures.

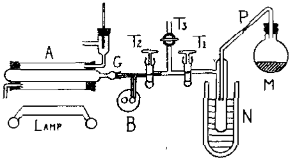
It was therefore considered of interest to investigate the photochemistry of glycxal vapour, especially as the results might eventually be expected to be of importance biochemically, as, for instance, in connexion with the problem of photosynthesis.

EXPERIMENTAL.

(A) *The Photochemical Decomposition.*

The photochemical experiments were carried out in the all-glass apparatus shown in Fig. 1. The monomeric glyoxal was prepared as required by heating a mixture of solid (polymeric) glyoxal and phosphoric oxide in the bulb *M*, after the method of Harries and Temme (*Ber.*, 1907, **40**, 165). The reaction gives rise to a mixture of carbon monoxide, carhon dioxide, and glyoxal vapour, and the last two were separated from the first by condensation in the liquid-air trap, *N*. When sufficient glyoxal had been prepared, the preparation bulb was sealed off at *P*, and the carbon monoxide pumped away from the trap by a Toepler pump *via* tap T_3. The trap was next surrounded by a freezing mixture of ice and hydrochloric acid at − 25°, a temperature at which practically all the glyoxal was retained whilst the carbon dioxide could he pumped away. The glyoxal was stored in the trap surrounded by liquid air, and could be kept thus for at least a day without much polymerisation.

FIG. 1.



The reaction chamber consisted of a glass, water-jacketed vessel, *A*, of 75 c.c. capacity, connected with the rest of the apparatus by the ground-glass joint, *G*, and kept at 25° by means of water pumped from an electrically regulated thermostat.

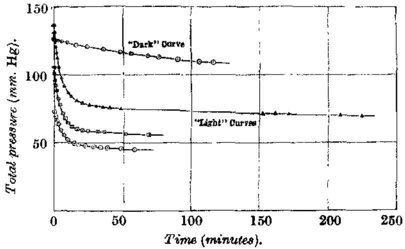
After complete evacuation of the apparatus, the glyoxal in the trap was allowed to attain room temperature, and the reaction chamber was filled to the desired pressure *via* taps T_1 and T_2,

pressures being measured on the mercury manometer, *B*. The vapour was then exposed to the action of light, and readings of the manometer were taken at short intervals of time.

In a preliminary experiment the unfiltered light from a 1000-c. p. filament lamp was used. The pressure in the reaction vessel decreased rapidly at first, and this rate of decrease diminished progressively with time.

The unfiltered light from a 3000-c. p. mercury-vapour lamp was used in all subsequent experiments, and in view of the fact that glass apparatus was employed, the light from the lamp in the regions 436, 405, and 365 $\mu\mu$ actually reached and was partly absorbed by the glyoxal. With this lamp the rate of decrease of pressure was greater than with the filament lamp, and the change

FIG. 2.



was nearly complete in 20 mins., but, although the pressure tended asymptotically to approximately half the initial value, even after 4 hours' illumination it did not quite reach this value. The filament lamp gave similar results. Typical curves are shown in Fig. 2.

The fall of pressure in the first half-minute was always less than in the succeeding half-minute, a fact which is probably due to a slight heating (Draper) effect owing to the onset of photochemical reaction in the vapour.

Over the major part of their courses the curves approximately conform to a bimolecular law with respect to the decomposing glyoxal. Table I shows some typical experiments at 25°, P_t being the observed pressure (in mm.) after t mins. of illumination, and k being the bimolecular velocity coefficient calculated from the equation $k = 1/P_0t . [(P_0 - P_t)/(P_t - \frac{1}{2}P_0)]$.

During the reaction the green colour of the glyoxal gradually faded and could not be detected after about 1 hour, while a glassy,

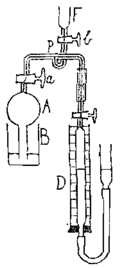
TABLE I.

t.	P_t.	$10^5.k$.	P_t.	$10^5.k$.	P_t.	$10^5.k$.	P_t.	$10^5.k$.	P_t.	10^5.
0	53·5	—	72·5	—	105	—	126·2	—	132·7	—
2	50·5	118	66·3	145	93·9	126	111·0	127	116·5	122
4	47·5	140	61·5	152	84·6	150	101·2	130	105·7	129
6	44·7	155	57·4	165	79·0	156	94·8	131	97·7	140
8	43·0	155	54·8	166	74·9	159	89·2	140	92·5	145
10	41·5	154	52·8	165	72·3	157	85·8	141	89·1	144
12	40·2	155	51·5	159	70·4	153	83·4	139	86·2	147
15			50·0	151	68·2	148	81·0	133	83·3	146
20			48·7	133	66·0	137	78·4	124	80·8	135

white solid appeared chiefly on the lower surface of the reactio vessel.

The residual gas at the end of the reaction was pumped out an analysed as described below; subsequent illumination of th residual solid failed to produce any further gaseou products.

FIG. 3.



In view of the fact that glyoxal vapou polymerises slowly (Harries and Temme, *loc. cit.* Harries, *Ber.*, 1913, **46**, 294), a blank run wa carried out in which the vapour was not illumin ated. The rate of decrease of pressure was sma compared with that observed when the vapou was illuminated, as is seen from the "dark" curve shown in Fig. 2.

Analysis of Gaseous Products.—The analysis o three samples of gas collected at the ends of th several runs gave quite concordant results (Tabl II), and was carried out in an apparatus (Fig. 3 adapted from that used by Dr. M. Brunner (privat communication), to whom we wish to express ou thanks.

The bulb, *A*, could be filled with mercury from the beaker, *B* by connecting the wide-mouthed tube, *F*, to a filter pump an opening taps *a* and *b*. The gas was passed from the burette, *D* to the bulb, *A*, where it was subjected to the action of the requisit reagent, which had been previously introduced into *A* by a pipett with a bent jet. Water introduced from *F* was used for washin the gas before the volume was finally measured in *D*. The forn of the bent T-piece, *P*, prevented any gas bubbles from collectin at this joint.

TABLE II.

Gas.	I.	II.	III.
CO	97·0%	97·0%	96·5%
H_2	2·7	2·5	2·5
Unsaturated compounds	0·3	0·4	0·9
Total	100·0	99·9	99·9

It appears from these results that under illumination from the mercury-vapour lamp, through glass, glyoxal decomposes in the main according to a bimolecular reaction, two volumes reacting to give one volume of carbon monoxide and a solid product. We may therefore write the empirical equation

$$2C_2H_2O_2 = CO + C_3H_4O_3 \quad . \quad . \quad . \quad . \quad (1)$$

The fact that hydrogen is also found to a small extent in the decomposition products suggests the reaction

$$C_2H_2O_2 = H_2 + 2CO \quad . \quad . \quad . \quad . \quad (2)$$

and the relative quantities of carbon monoxide and hydrogen in Table II show that about 98·5% of the decomposition may be represented by reaction (1) and 1·5% by reaction (2). The occurrence of reaction (2) would further account for the fact that the exact ratio of 2 : 1 for the initial to final pressures was never quite reached.

Although these equations satisfactorily represent the observed course of the reaction, it seemed possible, as an alternative, that glyoxal might exist as an equilibrium mixture of whole and half molecules $C_2H_2O_2$ and ·CHO (compare N_2O_4 and NO_2), and if this equilibrium were largely in favour of dissociation the facts might be represented by the equation

$$2CHO = CO + CH_2O \longrightarrow \text{[polymerised product]} \quad . \quad (3)$$

This view was tested by a determination of the vapour density of glyoxal. By weighing a dry bulb of known volume first full of air, and then full of glyoxal vapour at a known temperature and pressure, the molecular weight was found to be 58·7, corresponding closely to the formula $C_2H_2O_2$ (Calc.: *M*, 58·0), and therefore renders inadmissible any explanation of the facts based on thermal dissociation of the glyoxal.

(B) *The Nature of the Solid Product.*

The white solid produced in the reaction vessel was difficult to separate, since it adhered strongly as a glassy skin to the surface. It was slowly but extremely soluble in water, and easily soluble in alcohol, producing uncrystallisable solutions. It was slightly soluble in ether and acetone and insoluble in benzene. On heating, it decomposed without melting at 200°. It was somewhat hygroscopic, and always acquired moisture during attempts to scrape it from the surface of the vessel. In the earlier work it was therefore extracted by absolute alcohol, the solvent being subsequently removed as completely as possible by distillation first under reduced pressure at 30° and finally at 60° under a high vacuum.

It was fonnd, however, that the weight of solid extracted in this way was always somewhat greater than that to be expected from equation (1) and the known quantities of glyoxal reacting, and it seemed probable that some combination had occurred between the original solid and the alcohol, a conclusion which received further confirmation from the analytical data below. Moreover, the alcoholic extract was mnch more hygroscopic than the original white solid.

In later work, the white solid was removed from the reaction vessel by cutting the latter into sections and scraping vigorously with a sharp knife. The *substance* so obtained was then dried to a constant weight at 75°/1 × 10^{-4} mm., whereby it lost 3·1% of its weight during 2 days (Found, for dried material: C, 40·5; H, 4·3. $C_3H_4O_3$ requires C, 40·9: H, 4·6%).

The *substance* extracted by alcohol was analysed by three separate micro-estimations, two of which were kindly carried out for us by Professor Haworth, F.R.S. (Found: C, 42·8, 42·6, 42·4; H, 5·7, 5·6, 5·5. $C_{11}H_{18}O_{10}$ requires C, 42·6; H, 5·8%), and it therefore seems clear that the composition of the product is changed by reaction with alcohol during the process of extraction.

Molecular Weight.—The molecular weight of the solid in aqueous solution was determined by the Beckmann freezing-point method. On account of the small amount of material available it was necessary to work with solutions of about 0·05 g. of solid in 7 g. of water. Control experiments on similar quantities of purified glucose ($C_6H_{12}O_6,H_2O$) or sucrose and water constantly gave results for the molecular weights within 8% of the theoretical. Three series of determinations with the solid scraped from the reaction tube gave 332, 365, and 342 for the initial value of the molecular weight. This value decreased progressively with time until, in the latter two cases, final constant values of 90·8 ± 5 and 89·5 ± 5 were obtained. The following figures indicate the results of a typical experiment, the temperature being raised to 16° between each determination:

Wt. of solid, 0·0424 g.; wt. of water, 6·59 g.

Age of solution (mins.)	30	70	100	150	220	270	∞
Mean lowering of f. p.	0·035°	0·0525°	0·055°	0·0605°	0·069°	0·077°	0·134°
Molecular weight	342	288	218	198	173	155	89·5

Since the molecular weight of $C_3H_4O_3$ is 88, it appears that the polymeric substance deposited in the reaction vessel changes in solution to give the monomeric form. In view of the slow rate of solution, an hour being sometimes required at room temperature,

it is not possible to make any certain deductions as to the molecular weight of the polymerised form, for considerable depolymerisation may have occurred before the initial readings are taken.

Further determinations were carried out on the alcoholic extract; two experiments gave mean values of 300 and 308, whence, in conjunction with the analytical data, we conclude $C_{11}H_{18}O_{10}$ or $(C_3H_4O_3)_3,C_2H_6O$ (Calc.: M, 310) to be the formula of the extracted solid. The molecular weight of this substance changed on standing, giving final values of 98 ± 5 and 102 ± 5, and attaining the final value more quickly if the solution was warmed to 35°. This figure is somewhat higher than that for the white solid itself, a result which suggests that the molecule of alcohol associated with the polymerised molecule remains attached to one of the depolymerised forms, so that the apparent molecular weight falls to one-third of its original value.

Pseudo-acidic Character of the White Solid.—In an aqueous solution of the solid scraped from the reaction vessel, a gradual development of acidity occurred, even when the solution was kept in an atmosphere of hydrogen. This slow change took place at the ordinary temperature over a period of weeks, and was later traced to the fact that the monomeric product exists in two forms, one of which is strongly acidic. The equilibrium mixture of the two exhibits the phenomenon of progressive neutralisation similar to that described by Kling (*Compt. rend.*, 1905, **140**, 1256) for hydroxyacetone, the slow development of acidity being due to the slowness of the change of the non-acidic to the acidic form. This change takes place much more rapidly at higher temperatures, and complete titration of the mixture can be effected in less than an hour at 100°. In these experiments, the most satisfactory end-point was obtained with litmus, although fairly satisfactory results were also obtained with phenolphthalein.

As an example, the following experiment may be recorded: A solution of 0·0258 g. of the white solid in 10 c.c. of water required 0·9 c.c. of $N/20$-sodium hydroxide for neutralisation (litmus). On continued boiling, the titre increased progressively to a final value of 5·15 c.c. in the course of 1 hour. These figures give an initial equivalent of 570 and a final equivalent of 100, but slight decomposition had occurred at the end of the experiment. Another experiment, with smaller quantities and $N/100$-alkali, gave an initial equivalent of 440 and a final value of 88, whilst a third experiment gave 650 and 86, respectively. The first and third experiments were made with fresh solutions; the second, however, was done with a solution which had stood for 13 days and in which equilibrium had probably become established. Therefore, if 440

and 88 be taken as the most probable initial and final equivalents, it would appear that at equilibrium about 20% of the dissolved *substance is in the acid form.*

The equivalent of the acid form was further measured by heating the white solid under reflux on the water-bath with excess of sodium hydroxide for about 40 mins. Back titration with standard hydrochloric acid gave values of 94 ± 10 and 99 ± 10 for the equivalent. The results of these and the previous experiments are not quite accurate owing to the fact that the white solid is slightly decomposed by continued boiling, giving a brown solution, but the values obtained are in sufficiently close agreement with the theoretical value of 88 for $C_3H_4O_3$, and with the cryoscopic value of 90.

The evidence for the tautomerism of the monomeric substance in solution is further supported by an instantaneous reversible colour change which the solution undergoes on treatment with acids and alkalis. A drop of *N*-sodium hydroxide produces a bright yellow coloration which is immediately discharged on neutralisation by *N*-hydrochloric acid. This colour change can be repeated in the same specimen indefinitely. In addition, bromine water added to the aqueous solution drop by drop is at first instantly decolorised, whilst further quantities react slowly.

The sodium salt was prepared by dissolving together equivalent quantities of the white solid and sodium carbonate in the smallest possible quantity of water. The whole was kept at 60° for 6 hours, the colour of the solution turning gradually from lemon-yellow to dark red. A drop of this red solution on dilution gave a lemon-yellow solution, the colour of which was discharged by acidification with hydrochloric acid, and it was therefore concluded that the development of the red colour corresponded with the progressive neutralisation of the pseudo-acid and the gradual increase in concentration of its sodium salt. When the red solution was allowed to evaporate slowly in a desiccator over phosphoric oxide, it gradually became more viscous, and finally dried to a red, glassy substance without crystallising. This product was very hygroscopic, absorbing water from the air to form a red, treacly mass. In dilute solution it was yellow, the colour being discharged by acidification.

Reducing Properties of the White Solid.—The aqueous solution, in addition to its action with bromine water, showed other strong reducing actions. It apparently converted ferric into ferrous chloride, and reduced Benedict's and Fehling's solutions in the cold, thus differing from glyoxal, which does not react with Fehling's solution. These reactions indicate the existence of an aldehyde group in the molecule, and this conclusion was confirmed by the

observation that the solution readily reacts with phenylhydrazine (see below). The aldehyde group was estimated by the method of Cumming, Hopper, and Wheeler (" Systematic Organic Chemistry," 1923, 479) : an excess of standard potassium bisulphite was added to a known quantity of the aqueous solution of the " alcoholic extract," and the excess titrated with iodine. Two separate determinations gave equivalents of 102 and 96 referred to one aldehyde group, in good agreement with the theoretical value $\frac{1}{3} \times 310 = 103$ for the depolymerised form of the alcoholic extract.

These results are satisfactorily explained if, by analogy with Kling's formulæ for hydroxyacetone, (I) and (II), we adopt the

(I; neutral.) (II; acid.) (III; neutral.) (IV; acid.)

formulæ (*III*) and (*IV*) as representing the desmotropic forms of the monomeric glyoxal product. The source of the acidity is to be sought in the hydroxymethylene group, of which the tendency to develop strongly acidic properties when in combination with two electronegative groups is well known. For example, hydroxyacetone, hydroxymethylenecamphor, acetylacetone, acetoacetic and malonic esters all approach, and in some cases surpass, the monocarboxylic acids in strength, and may be represented as derivatives of formic acid by the general structure CXX′:CH·OH (Claisen, *Annalen*, 1897, **297**, 1; *Ber.*, 1893, **26**, 2731). Just as in the case of hydroxyacetone, however, so in the present instance, the change of the neutral into the acid form is slow, so that complete neutralisation by alkali only takes place gradually.

The *micro-preparation* of the following derivatives confirms the structure assigned to the decomposition product.

Quinoxaline Derivative.—0·04 G. of the white solid was dissolved in 1 c.c. of water, kept at 40° until depolymerised, mixed with 0·05 g. of recrystallised *o*-phenylenediamine dissolved in 1 c.c. of water, and the whole warmed to 60°. The yellow precipitate which formed rapidly was recrystallised from aqueous alcohol, and then had m. p. 165° (Found, by microanalysis : N, 15·3. $C_9H_8ON_2,H_2O$ requires N, 15·7%); it was somewhat soluble in both hot and cold water, and dissolved easily in dilute hydrochloric acid to give a brown solution from which it was reprecipitated by soda. This condensation may be taken as proof of the juxtaposition of two carbonyl groups in the molecule.

Reaction with Phenylhydrazine.—The aqueous solution of the white solid when added to a solution of redistilled phenylhydrazine

in 50% acetic acid gave *in the cold* a bright yellow precipitate which, when separated and recrystallised from aqueous alcohol, had m. p. 161° (Found, by microanalysis : C, 70·3; H, 5·9; N, 23·0. Calc. for $C_{21}H_{20}N_6$: C, 70·8; H, 5·6; N, 23·6%). If the reaction was carried out on a water-bath, the yellow precipitate first obtained rapidly turned brownish-red, and after recrystallisation from aqueous alcohol melted at 132° (Found : C, 70·2; H, 5·8; N, 23·0%). It would appear that these two products have the same composition.

The triphenylhydrazone of mesoxalic dialdehyde,

$$NHPh\cdot N{:}C(CH{:}N\cdot NHPh)_2,$$

has been obtained by von Pechmann (*Ber.*, 1891, **24**, 3257) as a yellow substance, m. p. 166°, and by Harries and Türk (*Ber.*, 1905, **38**, 1636) as a brown substance, m. p. 156°; but in view of the method of preparation used by von Pechmann, it seems that his compound is better represented by the isomeric azo-formula $NHPh\cdot N{:}C(CH_2\cdot N{:}NPh)_2$. It is therefore probable that our condensation products consist largely of these two isomeric substances.

As has already been seen, however, the white solid in solution gives an equilibrium mixture of two isomeric substances, and the possibility of the formation of the monophenylhydrazone of the *aci*-form, which is present to the extent of about 20%, must not be overlooked. The product of reaction with phenylhydrazine would thus contain a small quantity of the substance

$$NHPh\cdot N{:}CH\cdot C(OH){:}CH\cdot OH\,;$$

indeed, an admixture of 7% of this compound with the triphenylhydrazone would have the composition C, 70·1; H, 5·6; N, 23·0%, which is in close agreement with the analytical figures given above. A partial confirmation of this view was obtained by the observation that a small portion of both the yellow and the red product could be extracted by cold sodium hydroxide to give a yellow solution. Acidification turned this solution cloudy and discharged its colour, which was regenerated by the addition of alkali. Continued action of caustic soda on the original phenylhydrazine derivatives did not extract any further material, so it appears probable that it is the monophenylhydrazone of the enolic form which is thus extracted

The reaction with phenylhydrazine is in agreement with the formulæ proposed for the white solid if we assume that the predominant (non-acidic) form of the latter is capable of undergoing an "osazone" oxidation to form the triphenylhydrazone in the cold, and that at the same time the *aci*-form reacts to form a monophenylhydrazide in smaller quantity. This result is consistent with the fact that the rate of change of the one form of the white solid into the other is very slow.

Reaction with Hydroxylamine.—0·093 G. of the white solid, dissolved in 0·5 c.c. of water, was mixed with 0·16 g. of hydroxylamine hydrochloride dissolved in 0·5 c.c. of water and warmed; the mixture turned brown. 0·12 G. of sodium carbonate in 1 c.c. of water was then added, and after the effervescence had subsided the solution was warmed and allowed to stand for 24 hours. Two extractions of the clear brown solution with ether then yielded 0·053 g. of a white solid, m. p. 168° (decomp.) after drying under a high vacuum. It was soluble with difficulty in water and dilute hydrochloric acid, but easily soluble in soda. Its aqueous solution produced a dark red colour on warming with dilute cobalt acetate in the presence of sodium acetate, and sodium hydroxide then precipitated a green base, which redissolved to a dark red solution on acidification with hydrochloric acid. In all these respects the product acted like a glyoxime and it is believed that its structure corresponds to hydroxymethylglyoxime, $CH_2(OH)\cdot C(:N\cdot OH)\cdot CH:N\cdot OH$.

(C) *The Kinetics of the Change.*

The absorption spectrum of glyoxal in the blue, violet, and near ultra-violet shows fine structure (see p. 2830), and in accordance with spectroscopic theory we must conclude that no spontaneous dissociation of the molecule takes place as the result of light absorption. The alternative, that a molecule of photo-activated glyoxal reacts with an inactive molecule, is therefore to be preferred, and the bimolecular nature of the reaction shows it to be conditioned by the probability of collision between active and inactive molecules. Thus, if g and g' represent the concentrations of inactive and active glyoxal molecules respectively, we have, at equilibrium

$$dg'/dt = k_1Ig - k_2gg' - k_3g' = 0,$$

where k_1 refers to activation, k_2 to reaction, and k_3 to deactivation of glyoxal molecules, and I represents the intensity of illumination. Hence $g' = k_1Ig/(k_2g + k_3)$, and the rate of reaction of glyoxal is therefore

$$-dg/dt = k_2gg' = k_1k_2Ig^2/(k_2g + k_3)$$

whence, if k_3 is large compared with k_2, the measurable reaction will be approximately bimolecular.

The final elucidation of the mechanism must await a further investigation of the quantum kinetics of this reaction, which is now being carried out.

Summary.

Glyoxal gas decomposes in the light of the mercury vapour lamp, probably through the agency of the blue, violet, and ultra-violet light at 3650 Å.U. The main reaction involves a bimolecular

change, two volumes of glyoxal giving one volume of carbon monoxide and a polymerised solid product :

$$2C_2H_2O_2 = CO + (C_3H_4O_3) \longrightarrow \text{[polymerised product]}.$$

A second reaction to the extent of about 1·5% of the total change probably occurs with the production of hydrogen :

$$2C_2H_2O_2 = 2CO + H_2.$$

The solid product and its derivatives have been investigated, and its chemical properties, composition, and molecular weight are in accord with its representation as a polymeride of the hitherto unknown glycerosone to which it is hydrolysed in aqueous and acid solution.

The properties of glycerosone further suggest that in aqueous solution it exists in tautomeric equilibrium with an acidic hydroxymethylene form (III and IV), in analogy with other substances of this type.

The kinetics of the photochemical reaction is discussed.

We desire to express our thanks to Sir Robert Robertson, F.R.S., for granting facilities to one of us (J. G. A. G.) for continuing the cryoscopic experiments at the Government Laboratory. Our thanks are also due to the Governing Body of Emmanuel College, Cambridge, for assistance towards the maintenance of one of us (J. G. A. G.) while the work was in progress.

Department of Physical Chemistry,
Cambridge University. [*Received, August 13th, 1928.*]

CCCLXXIV.—*On Active Nitrogen. Part VI. The Formation of Iron Nitride in the Iron–Nitrogen Arc.*

By Eric John Baxter Willey.

In the course of an investigation upon the causes of brittleness in electric arc welds, it was found (Willey, *J. Soc. Chem. Ind.*, 1924, **43**, 263) that when an arc is burned between poles of iron in an atmosphere of nitrogen the deposit forming on the walls of the vessel contains iron nitride to the extent of *ca.* 2%. Moreover, the electrodes absorbed nitrogen and retained it very tenaciously. It was suggested that this is due to the formation of iron nitride through the interaction of active nitrogen and iron vapour or the finely divided metal evaporated from the electrodes, and Dr. Rideal later pointed out to the author that this comparatively small nitride content

might be greatly increased if the vapours were quickly removed from the high-temperature zone and chilled to prevent a subsequent decomposition of the nitride, which is known to be somewhat unstable. Fowler (J., 1901, **79**, 285) found that Fe_4N_2 begins to decompose into its elements at about 600°, but Noyes and Smith (*J. Amer. Chem. Soc.*, 1921, **43**, 475) have shown that the equilibrium nitrogen pressure for the same substance is about 41,000 atmospheres at 460°, good agreement being obtained between the observed values and those calculated by an application of the Nernst heat theorem to the data of Fowler and Hartog (J., 1901, **79**, 299) upon the heat of formation of Fe_4N_2 (3040 cals./g.-mol.) Hägg, however (*Nature*, 1928, **121**, 826), has concluded from *X*-ray examinations that this "nitride" is not a definite compound but rather a solid solution of nitrogen in iron (compare Fry, *Krupp'sche Monatsh.*, 1923, **4**, 137; *Stahl u. Eisen*, 1923, **43**, 1271). The matter was therefore shortly investigated and Rideal's prediction verified.

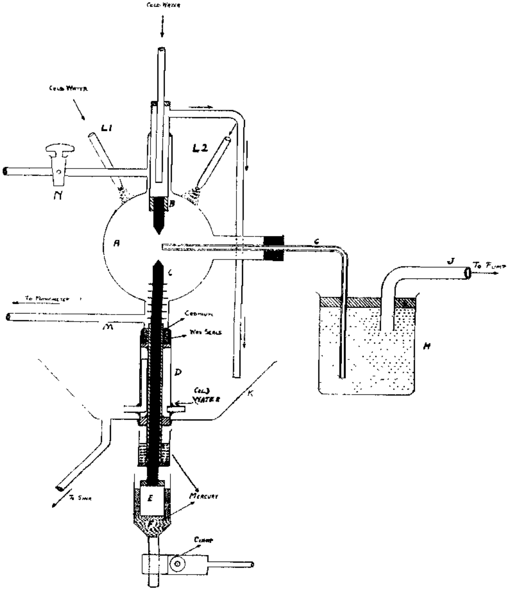
EXPERIMENTAL.

Nitrogen, purified and freed from oxygen by either hot copper or phosphorus, was led to the quartz globe, *A*, which was provided with three arms each with side tubes as shown. The upper electrode, *B*, was of Armco iron rod, about $\frac{1}{8}''$ in diameter and screwed into the solid ends of the $\frac{1}{2}''$ brass rod, which was bored out and fitted for water cooling as shown. The lower electrode, *C*, passed first through the water-cooled gland, *D* (made by accurate boring of another brass rod), provided with a mercury seal carried on the electrode as shown; access of mercury vapour to the bulb was prevented by a few carefully packed fragments of cadmium metal above the gland. Cooling fins on the electrode dissipated so much heat that the rod below *D* was rarely more than just warm, even when no water-cooling was employed on the gland. The steel float, *E*, rested on mercury in the column *F*, the height being adjustable by a levelling tube and reservoir. At *G* a quartz capillary, of 1·5 mm. bore, led to the stoppered litre beaker *H*, which was loosely packed with glass wool and fitted with an outlet tube, *J*, through which the nitrogen was drawn to a motor-driven oil pump of large capacity. The capillary was adjusted in trial runs so that it was in contact with the particular zone of the arc from which it was desired to draw the vapours. The electrodes and gland were fixed in position with Faraday wax, as was the tinned-iron funnel, *K*, to which the cooling water flowed; the bulb itself was also cooled by jets of water at *L*1 and *L*2. A manometer was also provided for the tube *M*.

Starting of the arc was effected by raising the reservoir *F*, until

the electrodes made contact; the level was then quickly dropped. It may be mentioned that, as found before, the arcs did not burn well after about an hour or so; this is clearly due to changes in the composition of the electrode tips owing to absorption of nitrogen, leading to a decrease in their ability to emit electrons and to give

FIG. 1.



iron vapour, which carries a large proportion of the current in the arc.

In the experiments, the tap, *N*, was closed, and the pump started to evacuate the system to 0·5 mm., the mercury reservoir being lowered, after which *N* was opened, nitrogen admitted, and the flow adjusted until a rate of 10 litres per hour was obtained, the

ressure being about 730 mm. The arc was then struck and allowed) burn until a suitable quantity of the iron–iron nitride mixture ad collected in H, after which the experiment was stopped.

The deposit was then separated from the glass wool by means of magnet, or in some cases the mixed wool and deposit were eighed, and treated with dilute sulphuric acid, and the wool was eparated by decantation, washed until no iron remained, dried ioroughly and reweighed, the amount of deposit being obtained by ifference. The iron was determined by permanganate and the itrogen by a Kjeldahl method, the ammonia in the distillate being ther titrated back with $N/50$-alkali (methyl-red being used as idicator), or, if the samples were small, determined colorimetrically; ie results were calculated to iron and iron nitride.

The amount of nitride present decreased from the metal-vapour one outwards; at the edge of the brilliantly blue inner zone of the rc 12—15% of the iron was present as nitride, Fe_4N_2, whilst at the iter edge of the arc the proportion had fallen to 6—8%, and the iblimate obtained from the walls of the bulb when a gentle ream of gas (1—2 litres per hour) was maintained contained ome 2—3%, as found in the previous experiments. Preliminary udies of the effect of power input on the yields showed that, hilst the distribution did not alter much, the actual quantities of itride obtained from an arc of 1·5 cm. length varied roughly as the nperage; the currents employed were from 3—10 amps. at 35 volts id upwards.

Discussion.

The principal interest of these results lies in their bearing on the xperiments in which evidence was obtained that nitrogen may be iemically active and yet show no luminosity (see Part IV, J., 1927, 331). These have recently been largely confirmed by Kaplan and ario's observation (*Nature*, 1928, **121**, 906) that the D lines in the idium spectrum can be excited by the non-luminous active trogen, of which the existence had been inferred by the present ithor from the ability of the gas to react with nitric oxide and idergo its characteristic exothermic catalytic decay at copper xide surfaces even when no glow is visible.

The arc in nitrogen is a brilliant bluish-white, with a reddish iter zone which may easily escape detection by reason of its omparative faintness. Examination of the arc light by means of a ilger spectrometer showed that the bands (especially in the yellow) hich are characteristic of the nitrogen afterglow spectrum could ot be detected visually; they may have been masked by the iron ies which are abundantly developed, but as these are comratively few in the yellow, the afterglow bands would have been

expected to appear. It may be that the reaction between the active nitrogen and the iron is so rapid that the quantity of the former present in the free state remains very low and hence cannot be seen, but the failure to obtain evidence of a glow would suggest either (1) that if the Rayleigh nitrogen be the active form it is here non-luminous, or (2) that, under the more intense mean-current and temperature conditions obtaining in the arc as compared with the condenser discharge, another and chemically more active modification of nitrogen such as Lowry's (J., 1912, **101**, 1152) is being produced.

The author's acknowledgments are due to Dr. Rideal for suggesting this investigation, to Mr. R. E. Stonebridge, who made the gland and float system, and to his assistant, Mr. R. Southward, for the accompanying diagram.

The experiments were carried out in the Laboratory of Physical Chemistry, Cambridge, early in 1925, and, although they had to be abandoned whilst still incomplete, it is hoped that they may lead to further investigations on reactions in the electric discharge—a subject which promises to be of much interest.

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CCCLXXV.—*Acid and Salt Effects in Catalysed Reactions. Part XVII. The Variation of the Catalytic Activity of an Acid with its Concentration, and the Determination of Ionisation Constants.*

By Harry Medforth Dawson, George Vincent Hall, and Arthur Key.

The facts established by various workers in the investigation of the dependence of the catalysing power of an acid on its concentration (Goldschmidt, *Z. physikal. Chem.*, 1910, **70**, 627; Goldschmidt and Thuesen, *Z. Elektrochem.*, 1911, **17**, 684; Bredig, Millar, and Braune, *ibid.*, 1912, **18**, 535; Snethlage, *ibid.*, p. 539; Dawson and Powis, J., 1913, **103**, 2135; Taylor, *Medd. K. Vetenskapsakad. Nobel-Inst.*, **2**, 34, 35, 37) led to the view that the catalytic effects are jointly due to the action of the hydrogen ion and of the undissociated acid. The sum total of the evidence for this joint action was such as to afford a very substantial basis for what became generally known as the dual theory of acid catalysis. In particular, it may be recalled that observations on the acetone–iodine reaction

with acetic, chloroacetic, αβ-dichlorobutyric, dichloroacetic, and hydrochloric acids gave in all cases the same value for the catalytic activity of the hydrogen ion, whilst the coefficients for the undissociated acid molecules varied very largely according to the nature of the acid.

The dual theory marks a well-defined stage in the development of the modern view, according to which catalytic effects are to be attributed to positively charged " hydrogen " and similar complex kations, to neutral molecules, and also to negatively charged anions —in short, to all those molecular entities which may act either as proton donators or proton acceptors (compare Lowry, J., 1927, 2554; Brönsted, *J. Physical Chem.*, 1926, **30**, 777). For an aqueous solution which contains an acid HA and the corresponding anion A^-, the equation for the catalytic effect may be written

$$v = k_h[H^+] + k_a[A^-] + k_m[HA] + k_{OH}[OH^-] + k_w[H_2O] \quad . \quad (1)$$

in which the relative values of the respective catalytic coefficients vary widely with the nature of the catalysed reaction. It is possible, for instance, that k_{OH} may be of the same order of magnitude or millions of times greater than k_h, and that the action of the undissociated water molecules as measured by k_w may be negligibly small or may represent a very important part of the observed catalytic effect. In such circumstances, it is apparent that all acid-catalysed reactions do not lend themselves to the quantitative investigation of the individual catalytic effects which are produced by the undissociated acid HA and the corresponding anion A^-. Generally speaking, favourable conditions will not be attained if the ratios k_m/k_h and k_a/k_h are very much less than about 0·01.

For a given reaction, the magnitude of these ratios depends on the ionisation constant of the catalysing acid. As the ionisation constant increases, the value of k_m increases, whilst that of k_a diminishes. For very weak acids it may therefore be possible to determine k_a, but not k_m, whilst the converse may be true for relatively strong acids. The fact that the acetone–iodine reaction affords k_m/k_h and k_a/k_h ratios of suitable magnitude in the case of moderately weak acids is largely responsible for the discovery of those simple relations which have found expression in the generalised form of the catalytic catenary.

The results to be described are concerned with the catalytic activity of a series of acids of varying strength, and it will be shown that the change in the catalysing power with the concentration affords a measure of k_m and also a value for the ionisation constant of the acid. The measurements relate to the acetone–iodine reaction at 25°, and it may be noted at the outset that the maximum

value of k_a/k_h is about 0·01. On account of the autocatalytic action of the hydriodic acid which is produced in the reaction, it is not possible to determine with the requisite accuracy the initial reaction velocity when the ionisation constant of the catalysing acid is much less than $K = 10^{-5}$.

For a solution which contains c mols. of HA per litre, the equation for the reaction velocity may be written

$$v = k_h[H^+] + k_a[A^-] + k_m[HA]$$
$$= (k_h + k_a - k_m)[H^+] + k_m c \quad . \quad . \quad . \quad . \quad (2)$$

If the acid is sufficiently weak, the hydrogen-ion concentration for the range of solutions $c = 0·01$ to $c = 0·5$ is given with close approximation by $[H^+] = \sqrt{Kc}$, and equation (2) may be written

$$v/\sqrt{c} = (k_h + k_a - k_m)\sqrt{K} + k_m\sqrt{c} \quad . \quad . \quad . \quad (3)$$

according to which $v/\sqrt{c}$ is a linear function of $\sqrt{c}$. The slope of this line gives k_m, and its intercept on the zero ordinate yields $(k_h + k_a - k_m)\sqrt{K}$. As already indicated, k_a can be neglected without serious error, but if required its value can be determined by methods which have been previously described. Since k_h is known, it follows that the intercept affords a measure of the ionisation constant K. The accuracy of the value is obviously limited by the degree of approximation which is involved in the substitution of $\sqrt{Kc}$ for $[H^+]$, and the error thereby introduced increases with the magnitude of K. The value of K derived from equation (3) may, however, be used as a preliminary value in proceeding to the next step in the process of evaluation.

In this further step, the value of $[H^+]$ in equation (2) is assumed to be given by the mass-law expression $[H^+] = c\alpha = \sqrt{Kc(1 - \alpha)}$, where α is the degree of ionisation of the acid and K the ionisation constant derived from equation (3). From equation (2), which may be put in the form

$$v = (k_h + k_a)[H^+] + k_m[HA],$$

we then obtain by substitution for $[H^+]$

$$v/\sqrt{c(1 - \alpha)} = (k_h + k_a)\sqrt{K} + k_m\sqrt{c(1 - \alpha)} \quad . \quad . \quad (4)$$

which yields a straight line when $v/\sqrt{c(1 - \alpha)}$ is plotted against $\sqrt{c(1 - \alpha)}$. The intercept of this line on the zero ordinate obviously leads to a value of K which is greater than that derived from the graph corresponding with equation (3), and at the same time the increased value of the intercept implies a smaller value of k_m.

If necessary, the second value of K may be used to derive a new series of values of $\sqrt{c(1 - \alpha)}$, and the procedure followed in the

second stage may be repeated. When the strength of the acid is such that the relation $[H^+] = \sqrt{Kc}$ is not even approximately true, the first step in the process may be omitted and the catalytic data applied directly to equation (4) with values of $\sqrt{c(1-\alpha)}$ derived from an approximate ionisation constant afforded by conductivity or other measurements. It should be noted that equation (4) may be written in the alternative form

$$v/c\alpha = k_h + k_a + k_m c\alpha/K \quad . \quad . \quad . \quad . \quad (5)$$

according to which $v/c\alpha$ is a linear function of $c\alpha$. This form affords a convenient method for the determination of one of the quantities K or k_m if the other is known, but is not so suitable for the evaluation of both K and k_m.

The results which have been obtained in the application of the above method are shown in the following tables, of which the order is determined by the magnitude of K. The first line of figures gives the concentration of the acid in mols. per litre, the second gives the observed initial reaction velocity with an acetone concentration of 20 c.c. per litre, the third gives the values of $v/\sqrt{c}$ or $v/\sqrt{c(1-\alpha)}$, and the fourth the corresponding values calculated from equation (3) or (4).

Propionic Acid.

c	0·01	0·02	0·05	0·1	0·2	0·4	0·5
$v \cdot 10^6$	0·181	0·269	0·449	0·664	0·997	1·545	1·76
$v/\sqrt{c} \cdot 10^6$	1·81	1·90	2·01	2·10	2·23	2·44	2·49
$v/\sqrt{c} \cdot 10^6$ (calc.)	1·85	1·90	1·99	2·09	2·23	2·44	2·52

The slope of the line when $v/\sqrt{c}$ is plotted against $\sqrt{c}$ gives $k_m = 1{\cdot}10 \times 10^{-6}$, and the intercept on the zero ordinate $(k_h + k_a - k_m)\sqrt{K} = 1{\cdot}74 \times 10^{-6}$. Since $k_h = 465 \times 10^{-6}$ and $k_a = 4 \times 10^{-6}$, this gives $K = (1{\cdot}74/468)^2 = 1{\cdot}38 \times 10^{-5}$. The calculated values of $v/\sqrt{c}$ are those derived from $10^6 \times v/\sqrt{c} = 1{\cdot}74 + 1{\cdot}10\sqrt{c}$.

Acetic Acid.

c	0·01	0·02	0·05	0·1	0·2	0·4	0·8
$v \cdot 10^6$	0·216	0·317	0·512	0·770	1·17	1·79	2·85
$v/\sqrt{c} \cdot 10^6$	2·16	2·24	2·29	2·43	2·62	2·83	3·18
$v/\sqrt{c} \cdot 10^6$ (calc.)	2·14	2·20	2·31	2·44	2·61	2·86	3·22

The slope of the $v/\sqrt{c}$ and $\sqrt{c}$ line gives $k_m = 1{\cdot}35 \times 10^{-6}$ and the intercept $= 2{\cdot}01 \times 10^{-6}$. Since $k_a = 4 \times 10^{-6}$, $K = (2{\cdot}01/467)^2 = 1{\cdot}85 \times 10^{-5}$. The calculated values of $v/\sqrt{c}$ are those given by $v/\sqrt{c} \cdot 10^6 = 2{\cdot}01 + 1{\cdot}35\sqrt{c}$.

Succinic Acid.

c	0·01	0·02	0·05	0·1	0·2	0·4	0·5
$v \cdot 10^6$	0·388	0·588	1·030	1·80	2·47	4·02	4·74
$v/\sqrt{c(1-\alpha)} \cdot 10^6$	4·04	4·27	4·69	5·12	5·57	6·40	6·74
$v/\sqrt{c(1-\alpha)} \cdot 10^6$ (calc.)	4·11	4·29	4·65	5·04	5·60	6·40	6·72

The first-stage plot of $v/\sqrt{c}$ against $\sqrt{c}$ gives $k_m = 4{\cdot}35 \times 10^{-6}$ and $(k_h + k_a - k_m)\sqrt{K} = 3{\cdot}65 \times 10^{-6}$. Since k_a is approximately 1×10^{-6}, this gives a preliminary value of $K = (3{\cdot}65/462)^2 = 6{\cdot}24 \times 10^{-5}$. From this the values of $v/\sqrt{c(1-\alpha)}$ in the third line are derived, and the plot of these against $\sqrt{c(1-\alpha)}$ gives $k_m = 4{\cdot}30 \times 10^{-6}$ and the intercept $(k_h + k_a)\sqrt{K} = 3{\cdot}70 \times 10^{-6}$, from which $K = (3{\cdot}70/466)^2 = 6{\cdot}30 \times 10^{-5}$. The values in the last line are those calculated from $v/\sqrt{c(1-\alpha)} \cdot 10^6 = 3{\cdot}70 + 4{\cdot}30\sqrt{c(1-\alpha)}$.

β-Chloropropionic Acid.

c	0·01	0·02	0·05	0·1	0·2	0·5
$v \cdot 10^6$	0·473	0·710	1·20	1·81	2·79	5·02
$v/\sqrt{c(1-\alpha)} \cdot 10^6$	4·96	5·20	5·49	5·81	6·31	7·15
$v/\sqrt{c(1-\alpha)} \cdot 10^6$ (calc.)	5·03	5·19	5·49	5·83	6·31	7·28

The preliminary plot gives $k_m = 3{\cdot}85 \times 10^{-6}$ and $(k_h + k_a - k_m)\sqrt{K} = 4{\cdot}48 \times 10^{-6}$, whence $K = 0{\cdot}94 \times 10^{-4}$. From the latter the values of $v/\sqrt{c(1-\alpha)}$ in the third line have been derived, and the plot of these against $\sqrt{c(1-\alpha)}$ gives $k_m = 3{\cdot}7 \times 10^{-6}$ and $(k_h + k_a)\sqrt{K} = 4{\cdot}68$, or $K = (4{\cdot}68/465)^2 = 1{\cdot}01 \times 10^{-4}$. The numbers in the fourth line are those calculated by use of equation (4).

The value of $K = 0{\cdot}86 \times 10^{-4}$ obtained by Lichty (*Annalen*, 1910, **319**, 380) from conductivity data is less than those for β-bromopropionic acid ($K = 0{\cdot}98 \times 10^{-4}$; Walden, *Z. physikal. Chem.*, 1892, **10**, 650) and for β-iodopropionic acid ($K = 0{\cdot}90 \times 10^{-4}$; Ostwald, *ibid.*, 1889, **3**, 193), whereas the strength of corresponding halogen-substituted acids normally increases from the iodo- to the chloro-acid. The higher value derived from the catalytic data has been confirmed by new conductivity measurements, which for $v = 16$ to $v = 256$ gave $K = 1{\cdot}04 \times 10^{-4}$.

Glycollic Acid.

c	0·01	0·02	0·05	0·1	0·2	0·4	0·5
$v \cdot 10^6$	0·585	0·882	1·495	2·31	3·61	5·86	6·79
$v/\sqrt{c(1-\alpha)} \cdot 10^6$	6·20	6·50	6·86	7·44	8·18	9·35	9·68
$v/\sqrt{c(1-\alpha)} \cdot 10^6$ (calc.)	6·24	6·47	6·94	7·47	8·21	9·27	9·70

The first-stage plot gives $k_m = 6{\cdot}0 \times 10^{-6}$ and $(k_h + k_a - k_m)\sqrt{K} = 5{\cdot}40 \times 10^{-6}$, whence $K = 1{\cdot}38 \times 10^{-4}$. From this, the

alues of $v/\sqrt{c(1-\alpha)}$ in the third line are derived, and the graph f these against $\sqrt{c(1-\alpha)}$ gives $k_m = 5{\cdot}7 \times 10^{-6}$ and $(k_h + {}_a)\sqrt{K} = 5{\cdot}70 \times 10^{-6}$, whence $K = (5{\cdot}70/465)^2 = 1{\cdot}50 \times 10^{-4}$. The umbers in the fourth line are those derived from $v/\sqrt{c(1-\alpha)} \cdot 10^6 = {\cdot}70 + 5{\cdot}70\sqrt{c(1-\alpha)}$.

Chloroacetic Acid.

....	0·005	0·01	0·02	0·05	0·1	0·2	0·5
. 10^6	1·055	1·655	2·56	4·62	7·31	11·80	23·0
$/\sqrt{c(1-\alpha)} \cdot 10^6$	19·5	20·0	20·7	22·5	24·5	27·5	33·4
$\sqrt{c(1-\alpha)} \cdot 10^6$ (calc.)	19·3	19·9	20·85	22·65	24·7	27·6	33·4

In the case of chloroacetic acid the substitution of $\sqrt{Kc}$ for $[H^+]$ a very rough approximation, as seen when $v/\sqrt{c}$ is plotted against $\sqrt{c}$, for the points corresponding with the lower acid concentrations ll very considerably below the straight line which reproduces irly well the data for the three most concentrated solutions. This ne gives $k_m = 23{\cdot}5 \times 10^{-6}$ and $(k_h + k_a - k_m)\sqrt{K} = 16{\cdot}0 \times 10^{-6}$, hence $K = 1{\cdot}31 \times 10^{-3}$. From this preliminary value of K, e second stage of the process gives $k_m = 22{\cdot}3 \times 10^{-6}$ and $(k_h + k_a)\sqrt{K} = 17{\cdot}9 \times 10^{-6}$, whence $K = 1{\cdot}48 \times 10^{-3}$. The alues of $v/\sqrt{c(1-\alpha)}$ in the third line are derived from the latter nd the plot of these numbers against $\sqrt{c(1-\alpha)}$ yields $k_m = 22{\cdot}2 \times 10^{-6}$ and $(k_h + k_a)\sqrt{K} = 18{\cdot}1 \times 10^{-6}$, whence $K = 1{\cdot}51 \times 10^{-3}$. he figures in the fourth line are those given by $v/\sqrt{c(1-\alpha)} \cdot 10^6 = 3{\cdot}10 + 22{\cdot}2\sqrt{c(1-\alpha)}$. Repetition of the second-stage process ius makes but little difference to the values obtained for k_m and K, though chloroacetic acid is not an acid which can be regarded as eak.

In the following table, the results of the measurements are ımmarised, and for comparison the values of K derived from conuctivity measurements are added in the last column.

Acid.	$k_m \times 10^6$.	K (from catalytic data).	K (from conductivity).
ropionic	1·1	$1{\cdot}38 \times 10^{-5}$	$1{\cdot}4 \times 10^{-5}$
cetic	1·35	$1{\cdot}85 \times 10^{-5}$	$1{\cdot}85 \times 10^{-5}$
ıccinic	4·3	$6{\cdot}30 \times 10^{-5}$	$6{\cdot}55 \times 10^{-5}$
Chloropropionic	3·7	$1{\cdot}01 \times 10^{-4}$	$1{\cdot}04 \times 10^{-4}$
lycollic	5·7	$1{\cdot}50 \times 10^{-4}$	$1{\cdot}52 \times 10^{-4}$
ıloroacetic	22·2	$1{\cdot}51 \times 10^{-3}$	$1{\cdot}55 \times 10^{-3}$

From the table it is evident that k_m increases in general with the rength of the acid. The slightly anomalous value for succinic acid ay possibly be connected with the fact that this is dibasic and is other ways not directly comparable with the other members of

the series. In all cases the ionisation constants derived from the catalytic data are in close agreement with those given by the conductivity of the acid in dilute solution.

According to equation (2), the hydrogen-ion concentration is given by $[H^+] = (v - k_m c)/(k_h + k_a - k_m)$, and provided k_a and k_m are known, the ionisation constant may be derived by substitution of this value of $[H^+]$ in $K = [H^+]^2/(c - [H^+])$. The result is illustrated by reference to the data for glycollic acid :

c	0·01	0·02	0·05	0·1	0·2	0·4	0·5
$[H^+] . 10^3$ ...	1·15	1·67	2·64	3·79	5·38	7·80	8·58
$K . 10^4$	1·50	1·53	1·47	1·49	1·49	1·55	1·50

Consideration of the Factors which affect the Value of K.

The determination of K and k_m by the method based on equation (4) involves the assumption that the ionisation constant K and the catalytic coefficients k_h, k_a, and k_m are not affected by changes in the concentration of the acid. From experiments on the catalytic activity of acids in solutions of catalytically inert salts (Dawson and Key, this vol., pp. 1239, 1248), it would appear that k_h increases continuously with the salt concentration, whereas k_a and k_m are but slightly affected by changes in the ionic environment. These experiments show, further, that the ionisation constant K increases with the salt concentration to a maximum and then diminishes as the proportion of salt in the solution is further increased.

The ionic concentration of the salt-free solutions with which we are concerned in this paper increases with the total acid concentration, but, in general, the ionic strength ($\mu = c\alpha$) is less than 0·01. In these circumstances, there will be no appreciable alteration in the values of the several catalytic coefficients, but since the ionisation constant increases rapidly with the ionic concentration at low values of the latter, it may be anticipated that K will increase somewhat as the concentration of the acid increases. On the other hand, it is well known that the addition of non-electrolytes to the aqueous solution of a weak electrolyte reduces the ionisation of the latter, and this factor may be expected to play some part in the more concentrated acid solutions. It seems possible, in fact, that the constancy of K, which is indicated by the catalytic data, may be due in some measure to the opposite effects which are produced by the ionised acid and by the non-ionised acid respectively.

Since the thermodynamic ionisation constant K_a is given by

$$K_a = a_{H^+} . a_{A^-}/a_{HA} = (f_+ f_-/f_0) \times [H^+][A^-]/[HA]$$

in which f_0 is approximately equal to unity, the connexion between K and K_a may be written $K = K_a/f_+f_- = K_a/f_\pm^2$, where $f_\pm$ is the

mean activity coefficient of the ions. Furthermore, the relation between $f_{\pm}$ and the ionic strength μ may be expressed in the form $\log 1/f_{\pm} = a\sqrt{\mu} - b\mu$, in which the second term may be neglected for small values of μ and, in accordance with the Debye–Hückel theory, a may be given the value 0·5 when the ions concerned are univalent. On replacing the ordinary by the natural logarithm, we obtain $\log_e 1/f_{\pm} = 1{\cdot}15\sqrt{\mu}$, whence $K = K_a . e^{2{\cdot}30\sqrt{\mu}}$ or $\sqrt{K} = \sqrt{K_a} . e^{1{\cdot}15\sqrt{c\alpha}}$. When this is introduced into equation (4), the latter takes the form

$$v/\sqrt{c(1-\alpha)} = (k_h + k_a)\sqrt{K_a} . e^{1{\cdot}15\sqrt{c\alpha}} + k_m\sqrt{c(1-\alpha)} \quad . \quad (6)$$

If the limiting ionic strength is taken as 0·01, which is greater than that of any of the solutions used in the catalytic experiments, except for the more concentrated solutions of the chloroacetic acid series, the limiting value of $e^{1{\cdot}15\sqrt{c\alpha}}$ is approximately 1·12, which signifies that an increase of 12% in the value of $v/\sqrt{c(1-\alpha)}$ might conceivably be debited to the change in the ionic environment in proceeding from $\mu = 0$ to $\mu = 0{\cdot}01$. This increase of 12%, although only a small fraction (see tables) of the actually observed increase in $v/\sqrt{c(1-\alpha)}$, represents the maximum increase which can be attributed to the ionic effect, for it takes no account of the opposing influence of the second term in the equation $\log 1/f_{\pm} = a\sqrt{\mu} - b\mu$. The influence of the un-ionised acid in the more concentrated solutions is also ignored. So far as the present series of experiments is concerned, it is perhaps still more important to bear in mind that all the solutions examined contained a small quantity of potassium iodide (0·002 mol. per litre). The presence of the latter diminishes very appreciably the variation of K which may be attributed to the increasing concentration of the ions in passing from the weaker to the stronger solutions. This may be illustrated by reference to the specific case of propionic acid for which $e^{1{\cdot}15\sqrt{\mu}}$ increases from 1·058 for $c = 0{\cdot}01$ to 1·083 for $c = 0{\cdot}5$. The corresponding increase in $e^{1{\cdot}15\sqrt{\mu}}$ for glycollic acid is from 1·065 for $c = 0{\cdot}01$ to 1·12 for $c = 0{\cdot}5$. In such circumstances, it is not difficult to understand that the catalytic data are generally consistent with the assumption of a constant value for K.

In this connexion, attention may be directed to the experimental data obtained by Dawson and Powis (*loc. cit.*) for the much stronger dichloroacetic acid at concentrations between $c = 0{\cdot}01$ and $c = 0{\cdot}2$. In the application of equation (4) to these results, the values of $v/\sqrt{c(1-\alpha)}$ have been derived from $K = 5{\cdot}0 \times 10^{-2}$ (Drucker, *Z. physikal. Chem.*, 1904, **49**, 563):

Dichloroacetic Acid.

c	0·01	0·02	0·05	0·1	0·2
$v \cdot 10^6$	4·10	7·95	18·1	32·7	59·6
$c\alpha$	0·00854	0·0153	0·0309	0·0500	0·0780
$v/\sqrt{c(1-\alpha)} \cdot 10^6$	107·3	116·0	131·0	146·2	170·6
$v/\sqrt{c(1-\alpha)} \cdot 10^6$ (calc.)	110·6	116·7	130·6	147·7	172·8

The plot of $v/\sqrt{c(1-\alpha)}$ against $\sqrt{c(1-\alpha)}$ gives a straight line, the slope of which yields $k_m = 200 \times 10^{-6}$. The numbers in the last horizontal line are those derived from $v/\sqrt{c(1-\alpha)} \cdot 10^6 = 103{\cdot}0 + 200\sqrt{c(1-\alpha)}$. As in the case of the weaker acids, these results indicate that the catalytic data for dichloroacetic acid can be satisfactorily co-ordinated in terms of equation (4) with a constant value of K. It is to be noted, however, that the solutions of dichloroacetic acid contained a larger quantity of potassium iodide, *viz.*, 0·008 mol. per litre. This would certainly tend to reduce the influence of the ionised acid on the value of K. At the same time, the ionic strengths of this series of solutions (see third line of table) are of such magnitude that the second term in the equation $\log 1/f_{\pm} = a\sqrt{\mu} - b\mu$ cannot entirely be left out of account. Without entering into a more minute discussion of the matter in this paper, we would further suggest that it is improbable that the polarising influence of ionic environment, as measured by a, is independent of the nature of the positive and negative ions, even when these carry the same charge. There is, indeed, a substantial amount of evidence to support the view that such influence is specific even at very low ionic concentrations.

In conclusion, attention may be directed to the very general applicability of the catalytic method as a means of determining the degree of ionisation of an acid. If the values of k_h, k_a, and k_m are known, the method may be applied to solutions of the acid *in pure water or in solvents which contain relatively large quantities* of catalytically inert salts. The conductivity method fails completely when foreign electrolytes are present in more than very small amounts, and since the mobility of the ions is so largely affected by interionic forces, it is at the best limited to solutions of low ionic strength.

Summary.

The catalytic effects produced by propionic, acetic, succinic, β-chloropropionic, glycollic, and chloroacetic acids have been studied with reference to the variation of the catalysing power with the concentration.

It is shown that the connexion between the reaction velocity and the concentration affords a means of determining the ionisation

constant of the acid as well as the catalytic activity of the undissociated acid.

The ionisation constants derived from the catalytic data are in close agreement with those afforded by the electrical conductivity of dilute solutions of the acids.

In general, the catalytic activity of the undissociated acid increases with the ionisation constant.

The relation between the catalytically determined constant K and the thermodynamic constant K_a is considered in reference to the various factors which affect the value of K under the conditions which obtain in the experimental determinations.

THE UNIVERSITY, LEEDS. [*Received, August 22nd*, 1928.]

CCCLXXVI.—*The Reactions of Hydrogen Chloride with the Dioxides of Selenium and Tellurium between* 0° *and* 170°.

By THOMAS WALLACE PARKER and PERCY LUCOCK ROBINSON.

SELENIUM dioxide has been stated by Ditte (*Compt. rend.*, 1876, **83**, 56) to absorb hydrogen chloride exothermally, forming, (1) at the ordinary temperature, an amber-coloured liquid, SeO_2,HCl, stable below 26°, but evolving hydrogen chloride on warming, and (2) at low temperatures, a transparent yellow solid, SeO_2,2HCl, which reverts to SeO_2,HCl on rise of temperature. The formation of SeO_2,2HCl was confirmed by Lenher (*J. Amer. Chem. Soc.*, 1920, **42**, 2498), who, however, did not specify the temperature; by the action of either phosphoric oxide or calcium chloride on this compound, followed by distillation, he prepared selenium oxychloride.

The present authors find that a pale yellow solid approximating closely to SeO_2,4HCl is formed at 0°; when warmed, this loses hydrogen chloride, liquefies completely at 35°, and at 100° is a yellow liquid containing slightly more hydrogen chloride than required by SeO_2,2HCl. If the reaction is started at 18°, the resulting material is partly liquid, has the composition SeO_2,2·6HCl, and behaves like the preceding product when heated to 100°; whereas at 100° material identical with the previous final product is obtained. At 140—170° an amber-coloured liquid is formed of composition SeO_2,1·3HCl, which on distillation partly decomposes into selenium dioxide and hydrogen chloride, the resulting clear yellow liquid, b. p. 160—170°, d 2·45, having the composition SeO_2,1·8HCl. Redistillation of the liquid in a vacuum is accompanied by a further partial decomposition, producing a distillate, b. p. 70—80°/15 mm., the analysis of

which agrees with $SeO_2,2HCl$. We therefore conclude that there are two addition compounds, *viz.*, (1) $SeO_2,4HCl$, a yellow solid stable at 0°, and (2) $SeO_2,2HCl$, a yellow liquid, stable up to and partly distillable at 170°. This liquid dissolves hydrogen chloride in amounts varying with temperature.

Ditte (*Compt. rend.*, 1876, **83**, 336) considered that an addition compound, $2TeO_2,3HCl$, was formed by passing dry hydrogen chloride over tellurium dioxide at − 10°, which dissociated at the ordinary temperature, yielding TeO_2,HCl, but he obtained no evidence of $TeO_2,2HCl$ at an intermediate stage; TeO_2,HCl was described as beginning to lose water at 110° and yielding at 300° tellurium oxychloride, $TeOCl_2$, a yellow liquid setting to a crystalline solid. Lenher (*J. Amer. Chem. Soc.*, 1909, **31**, 243) found that the dioxide and hydrogen chloride combined to form $TeO_2,3HCl$ at 0°, and that this was successively converted into $TeO_2,2HCl$ and $TeCl_4$ on heating, but he obtained no evidence of the formation of tellurium oxychloride in any reaction. At 280—300° tellurium dioxide was completely volatilised in a stream of hydrogen chloride, presumably as tetrachloride and steam. The present investigation shows that at 0° hydrogen chloride is absorbed in varying quantities by the dioxide, giving a product, obviously not homogeneous, which loses water continuously with rising temperature when heated in a stream of the gas. There is no evidence that tellurium dioxide forms a definite addition compound within the range 0—150°, the experimental data according more closely with the anticipated behaviour of basic chlorides in the presence of hydrogen chloride.

EXPERIMENTAL.

Tellurium.—The dioxide was prepared by adding successive small quantities of finely powdered tellurium to boiling concentrated nitric acid, decanting the excess of acid, washing the oxide well with water and drying it first on a steam-bath and then at 110° (Found Te, 77·4. Calc. for TeO_2 : 79·9%). This material was used in the preliminary runs, but for the later work it was just fused and then allowed to crystallise, the central portions of the melt being used (Found : Te, 79·3%). Hydrogen chloride, dried and purified by passing successively through concentrated sulphuric acid and a cotton-wool filter, was led into a horizontal glass tube containing the dioxide (1—3 g.) in a porcelain boat at laboratory temperature. The oxide first turned yellow, then moist, and finally separated into yellow liquid and white solid layers; the solid lost 1·4% of moisture in a desiccator, but gained 12% on exposure to the air, dirty white friable solids being produced in each case. After various periods of passage of gas, the increase in weight of the contents of the boat

was irregular and neither the liquid nor the solid was of definite composition (see Table I).

TABLE I.

Run.	Time, hrs.	Increase in weight, %.	Empirical composition calc. from increase.	Liquid. Te %.	Liquid. Cl %.	Solid. Te %.	Solid. Cl %.
1	5	38·4	TeO_2,1·68HCl	30·7	29·0	—	—
2	7	35·8	TeO_2,1·57HCl	30·6	26·1	59·9	—
3	7	44·7	TeO_2,1·96HCl	—	—	—	—

Further experiments were made with the oxide in a stoppered U-tube at laboratory temperature and at 100°. Pure, dry hydrogen chloride was passed first through a weighed stoppered U-tube (*A*) with a filling of phosphoric oxide, then through the reaction tube, and finally through a second, weighed, stoppered U-tube (*B*) filled in like manner. The drying-tubes were filled with hydrogen chloride before all weighings and the weight of the reaction tube was corrected for the change from air to hydrogen chloride. Baker (J., 1898, 73, 422) has shown that unless phosphoric oxide is pure it absorbs small quantities of hydrogen chloride, and accordingly the difference between the increase in tubes *A* and *B* was taken as the amount of water leaving the reaction tube. Run 4 confirms Baker's observations, but in runs 5 and 6, carried out at 100°, it is obvious that the course of the reaction has changed; little hydrogen chloride has been absorbed, and some water, presumably that produced in the reaction, has been arrested by tube *B*. In these runs there was evidence of a slight reaction, the surface of the solid becoming greenish-yellow whilst a trace of brown sublimate was carried a little way up the limb of the reaction tube.

TABLE II.

Run.	Time, hrs.	Temp.	Weight of TeO_2, g.	Increase in weight, %.	Empirical composition calc. from increase.	Change in weight (g.) in *A*.	Change in weight (g.) in *B*.
4	5	18°	0·5564	40·4	TeO_2,1·77HCl	+0·0130	+0·0156
5	12	100	1·0420	6·3	TeO_2,0·27HCl	+0·0126	+0·0290
6	2·5	100	1·4154	9·3	TeO_2,0·41HCl	−0·0002	+0·0324

Three further runs (7, 8, 9) were carried out exactly as above in order to ascertain the change taking place in the material formed at 0° when it was subsequently heated in a stream of the gas. The reaction tube was first surrounded by a brine bath maintained at 0° ± 1° and gas was passed through the material for 5 hours. After the three U-tubes had been weighed the product was warmed to 100°, and subjected to the action of hydrogen chloride for a further 3 hours, and the tubes were re-weighed; finally, the temperature

was raised to 150°, and gas passed for a further 2 hours, after wh the last weighings were made. The results are shown in Table I from which it is clear that at the higher temperatures there is a l of water and a nearly equal gain of chlorine.

TABLE III.

Temp.	Run	7.	8.	9.	10.
0°	TeO_2, g.	0·8320	0·8922	0·3580	0·808
	Increase, %.	35·9	26·2	40·2	32·1
	HCl/TeO_2 (mols.)*	1·57	1·15	1·76	1·40
	Increase in A, g.	0·0408	0·0870	0·0830	0·006
	Increase in B, g.	0·0790	0·0996	0·0936	0·000
100°	Increase, %	35·7	29·7	47·7	41·5
	HCl/TeO_2 (mols.)*	1·56	1·30	2·09	1·82
	Increase in A, g.	*0·0082*	*0·0590*	*0·0682*	*0·003*
	Increase in B, g.	0·0370	0·1018	0·1014	0·030
150°	Increase, %.	33·8	30·7	51·3	47·0
	HCl/TeO_2 (mols.)*	1·48	1·34	2·24	2·05
	Increase in A, g.	0·0310	0·0438	0·0726	0·001
	Increase in B, g.	0·1152	0·1348	0·1216	0·036

* Calculated from increase.

At the highest temperature, water carried forward by the g stream was observed to condense in droplets in the connecting tub In run 10, which confirms the results in runs 7—9, drying tul filled with calcium chloride were used to confirm the conclusion th the increase recorded in the *A* tube when phosphoric oxide was us is due to the cause indicated above.

Tellurium was estimated by dissolving weighed amounts of t compounds in hot concentrated hydrochloric acid and addi successively a saturated solution of sulphur dioxide, a 15% soluti of hydrazine hydrate in hydrochloric acid, and finally more sulph ous acid; the resulting black colloidal tellurium was granulated boiling for 10 minutes and then weighed on a Gooch crucil (compare Gutbier and Huber, *Z. anal. Chem.*, 1914, **53**, 430).

Selenium.—Crude dioxide was purified by solution in concentrat nitric acid, evaporation to dryness, and gentle ignition. Calciu chloride drying-tubes were used, and runs were conducted exac as above at 0°, with change to 100°; at laboratory temperatu with change to 100°; and at 100° throughout. At 0° a very lig yellow solid was produced which developed a considerable pressu of hydrogen chloride at the ordinary temperature, and there was change in the weight of the *B* tube; on being heated to 100° th solid melted to a dark yellow liquid, and an increase was noted the *B* tube, but it appeared to be due, not to water, but to t distilling forward of the undecomposed compound, for the tu became yellow, and, moreover, when the increase in weight of the tube was added to the increase in the reaction tube, the sum alwa

indicated the presence of a substance having a composition very close to SeO_2,2HCl. At laboratory temperature a mixture of liquid and solid was produced which gave precisely similar results when heated to 100° in a current of hydrogen chloride. The product obtained directly at 100° behaved similarly. The results are given in Table IV.

TABLE IV.

Run.	SeO_2 (g.).	Increase % at 0°.	Increase % at 20°.	HCl/SeO_2 (mols.).	Increase at 100°, %.	HCl/SeO_2 (mols.).
11	0·3220	126·5	—	3·85	60·3	1·83
12	0·3142	131·9	—	4·02	66·7	2·03
13	0·1576	134·6	—	4·10	70·9	2·16
14	0·1620	127·7	—	3·89	81·9	2·50
Mean		130·2	—	3·97	70·0	2·13
15	0·1364	—	79·1	2·41	75·2	2·29
16	0·1468	—	90·2	2·75	(45·6)	(1·39)
Mean			84·7	2·58	75·2	2·29
17	0·1760	—	—	—	71·5	2·18
18	0·1574	—	—	—	70·7	2·15
Mean					71·1	2·17
General mean at 100°						2·16

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CCCLXXVII.—*The Production of Thiophen by the Interaction of Acetylene and Carbon Disulphide.*

By HENRY VINCENT AIRD BRISCOE, JOHN BUTTERY PEEL, and PERCY LUCOCK ROBINSON.

THE small proportion of thiophen that is formed, together with carbon disulphide, by the interaction of acetylene and sulphur vapour (Peel and Robinson, this vol., p. 2068) is produced probably by a direct reaction of acetylene with sulphur, and not by a secondary reaction between the gas and carbon disulphide, for the work described below indicates that thiophen is produced in quantity by the latter reaction only at temperatures considerably higher than those required when sulphur is used. The reaction of acetylene with carbon disulphide at 700° affords a convenient and cheap means of synthesising pure thiophen in quantity.

A rapid stream of acetylene, saturated with carbon disulphide vapour by passage through the boiling liquid, was delivered into the end of a horizontal silica tube (22 × 2 ins.), from which it passed through a water condenser to a collecting bottle. The tube could be maintained electrically at any desired temperature up to 800°, and the heated zone was packed with broken porous pot. Condensate from runs at specific temperatures was collected and separated into

its constituents by the careful fractionation previously described. At 200°, the liquid was entirely unchanged carbon disulphide; a trace of thiophen appeared at 350° and the quantity gradually increased with rise of temperature until at about 700° the condensate contained approximately 10% by volume of thiophen and about 10% of hydrocarbons. This was the maximum yield for the particular length of hot zone used, nor was it possible to increase the yield by employing bauxite or granular copper sulphide as the furnace packing. At temperatures higher than 700° the tube became choked with carbon before the amount of condensate was sufficient for investigation.

Acknowledgment is made of a grant from the Research *Fund* Committee of Armstrong College, which enabled one of us (J. B. P.) to take part in this work.

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CCCLXXVIII.—o-*Sulphinobenzoic Acid.*

By WILLIAM BENNETT PRICE and SAMUEL SMILES.

IN the course of experiments with hydroxy-derivatives of thioxanthone dioxide, *o*-sulphinobenzoic acid was required. Two methods are recorded for the preparation of this acid, either from *o*-diazobenzoic acid with sulphurous acid (Gattermann, *Ber.*, 1899, **32**, 1144) or from the dichloride of *o*-sulphobenzoic acid by reduction with alkaline sulphite (Davis and Smiles, J., 1910, **97**, 1290), but neither is suitable for the preparation of large quantities of the material, the yield being variable and the quality of the product, particularly when the latter method is used, often poor.

According to patent literature (D.R.-P. 35230), a solution of *o*-chlorothiolbenzoic acid is obtained when *o*-thiolbenzoic acid is treated with chlorine in presence of an inert solvent. No mention is made of the isolation of the chlorothiol, but assuming the formation of the substance, it was expected that on treatment with water the usual decomposition of chlorothiols observed by Zincke (for example, *Annalen*, 1918, **416**, 86) would ensue, yielding the sulphinic acid and the disulphide, the latter of which would be available for renewed treatment with chlorine. Accordingly, the action of chlorine on *o*-thiol- or *o*-dithio-benzoic acid in presence of carbon tetrachloride has now been more fully studied. As a result, although the *o*-chlorothiolbenzoic acid has not been encountered, good yields of an unstable *dichloro*-derivative have been obtained. This material,

when carefully treated with water, yields the almost pure sulphinic acid. As described in the experimental part, a trustworthy and simple method for preparing the acid is thus available.

The reactions of this dichloro-derivative have been further studied with the object of determining its structure. The halogen is entirely and quickly removed by ice-cold water; *o*-sulphinobenzoic acid alone is formed, no disulphide being observed. In fact titration with alkali hydroxide accords with the equation

$$C_7H_4O_2Cl_2S + 4NaOH = 2NaCl + 2H_2O + CO_2Na{\cdot}C_6H_4{\cdot}SO_2Na.$$

The substance might accordingly be represented in any of the three following ways:

$$C_6H_4{<}^{SOCl}_{COCl} \qquad C_6H_4{<}^{SO-}_{CCl_2}{>}O \qquad C_6H_4{<}^{SCl_2}_{CO-}{>}O$$

(I.) (II.) (III.)

but the acyl dichloride (I) and the *C*-dichloro-anhydride (II) structures are discarded for the following reasons. On treatment with *p*-nitrobenzyl alcohol a mononitrobenzyl ester was obtained together with *p*-nitrobenzyl chloride. The first-named product was evidently the *sulphinic ester* $CO_2H{\cdot}C_6H_4{\cdot}SO{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$ (IV), since it yielded the sulphinic acid on hydrolysis and differed from the *sulphone*, $CO_2H{\cdot}C_6H_4{\cdot}SO_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$ (V), which was obtained from the sodium sulphinate and *p*-nitrobenzyl chloride or by oxidation of the corresponding sulphide. Moreover, the substance did not react with *p*-benzoquinone in the manner characteristic of sulphinic acids (Hinsberg, *Ber.*, 1894, **27**, 3259), and of *o*-sulphinobenzoic acid in particular. On treatment with phenols this chloro-compound yielded hydroxy-derivatives of *o*-carboxydiphenyl sulphide (*e.g.*, VI) together with chlorophenols. Neither with alcohols nor with phenols has any evidence of the formation of carboxylic esters been discovered. The incompatibility of this result with the structures (I) and (II) is evident and it is emphasised by the behaviour of the isomeric chlorides of *o*-sulphobenzoic acid with these reagents (List and Stein, *Ber.*, 1898, **31**, 1648). Moreover, the formation of the acyl dichloride (I) or of the *C*-dichloro-anhydride (II) by the action of chlorine on *o*-thiol- or *o*-dithio-benzoic acid cannot be simply interpreted. On the other hand, the formation of the *S*-dichloro-anhydride (III) by the process is readily explained by assuming the loss of hydrogen chloride from the *o*-chlorothiol (VII) and the sub-

$$C_6H_4{<}^{S\cdot C_6H_4\cdot OH}_{CO_2H} \qquad C_6H_4{<}^{SCl}_{CO_2H} \qquad C_6H_4{<}^{S-}_{CO-}{>}O$$

(VI.) (VII.) (VIII.)

sequent addition of halogen to the sulphenic anhydride (VIII). For these reasons the substance is regarded as the *S*-dichloro-

anhydride and it is evident that the reactions with *p*-nitrobenzyl alcohol and with phenols accord with this structure. Bearing in mind the tautomeric behaviour of the two chlorides of *o*-sulphobenzoic acid (List and Stein, *loc. cit.*), it seems not improbable that under suitable conditions conversion into the acyl dichloride might be realised, but as yet this has not been effected and no evidence of tautomeric character has been discovered.

During the investigation of the sulphinic ester (IV) and the isomeric sulphone (V) the p-*nitrobenzylsulphone ester* (IX) was encountered. This substance is attacked by alcoholic sodium hydroxide, yielding the red sodium salt of 3-*keto*-2-p-*nitrophenyl*-2 : 3-*dihydrothionaphthen dioxide* (X; $R = C_6H_4{\cdot}NO_2$). Further investigation of this method of synthesising 2-derivatives of thionaphthen dioxide is being made; from sodium *o*-sulphinobenzoate and ethyl chloroacetate, 3-keto-2-carbethoxy-2 : 3-dihydrothionaphthen dioxide (X; $R = CO_2Et$) has already been obtained. This product is identical

$$\text{(IX.)}\quad C_6H_4{<}{\begin{matrix}SO_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2\\CO{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2\end{matrix}}\qquad\qquad C_6H_4{<}{\begin{matrix}SO_2\\CO\end{matrix}}{>}CHR\quad\text{(X.)}$$

with the " anhydro " derivative obtained by Feist (*Ber.*, 1925, **58** 2311) from the reaction of fuming sulphuric acid with ethyl benzoyl acetate. The structure assigned to the substance by Arndt (*Ber.* 1926, **59**, 1074), after examining the products of hydrolysis, is thu confirmed.

EXPERIMENTAL.

o-*Sulphinobenzoic Acid*.—Dry chlorine was passed into a mixtur of dry carbon tetrachloride (40 c.c.) and *o*-thiolbenzoic acid (10 g until the latter had dissolved. Dry air or nitrogen was passe through the clear solution until hydrogen chloride and the excess (chlorine had been removed. The dichloro-anhydride, which sepa ated in the crystalline state as a result of the fall in temperatu and loss of solvent, was collected and spread on porous earthenwar Atmospheric moisture liberated hydrogen chloride from the materia and this decomposition was completed by means of ice. Tl sulphinic acid was then obtained in the crystalline state (yield, c usu–70%), the crude product having usually m. p. 123—124°. Tl *Annale*:fied acid decomposed and solidified a few degrees above i and the ng point (126°; Gattermann, *loc. cit.*, gives m. p. 125°), formi renewed tre- and *o*-sulpho-benzoic acids. With impure samples tl on *o*-thiol- or ation may take place below the m. p., with the resu has now been material does not fuse until near the m. p. of *o*-dithiobenz thiolbenzoic acid This behaviour explains the high melting point record unstable *dichloro*-dic acid by Davis and Smiles (*loc. cit.*), their produ

obtained by reduction of o-sulphobenzoyl dichloride, being evidently impure.

The *dichloride* (III) of o-sulphinobenzoic acid was prepared as described in the foregoing paragraph, purified materials being used. Owing to the instability of the substance and its sensitiveness to moisture, further purification by recrystallisation could not be effected. It formed cream-coloured needles, m. p. 62° (Found : Cl, 29·9; S, 14·3. $C_7H_4O_2Cl_2S$ requires Cl, 31·8; S, 14·3%. $C_7H_5O_2ClS$ *requires* Cl, 18·8; S, 17·0%). Decomposition with aqueous sodium hydroxide gave equiv., 56·0. $C_7H_4O_2Cl_2S$, according to the equation given on p. 2859, requires equiv., 55·7.

p-*Nitrobenzyl* o-*Carboxybenzenesulphinate* (IV).—A solution of the dichloride (from 4·25 g. of o-thiolbenzoic acid) from which excess of chlorine and hydrogen chloride had been removed was mixed with a concentrated solution of p-nitrobenzyl alcohol in dry ether. The *ester* separated in the crystalline state and after suitable purification from ether it was obtained in needles, m. p. 121° (Found : C, 52·4; H, 3·2; N, 4·4; S, 10·0. $C_{14}H_{11}O_6NS$ requires C, 52·3; H, 3·4; N, 4·3; S, 9·9%). p-Nitrobenzyl chloride was isolated from the mother-liquors of the reaction. The ester did not attack a cold aqueous suspension of p-benzoquinone. A sample was hydrolysed by boiling water; the products—p-nitrobenzyl alcohol and o-sulphinobenzoic acid—were isolated and identified in the usual manner.

o-*Carboxyphenyl*-p-*nitrobenzylsulphone* (V) was obtained by boiling the potassium salt of o-sulphinobenzoic acid (1 mol.) and p-nitrobenzyl bromide (1 mol.) in alcohol which contained a little water. The potassium salt of the required acid separated from the cooled mixture. The *acid* was purified from aqueous acetic acid; it had m. p. 226° and was not attacked by aqueous sodium hydroxide (Found : C, 52·3; H, 3·4; S, 10·0. $C_{14}H_{11}O_6NS$ requires C, 52·3; H, 3·4; S, 9·9%).

The p-*nitrobenzyl* ester (IX) of o-carboxyphenyl-p-nitrobenzylsulphone was obtained when a concentrated alcoholic solution of potassium o-sulphinobenzoate (1 mol.) and p-nitrobenzyl bromide (2 mols.) was boiled for 2 hours. After purification from acetic acid the product formed plates, m. p. 190° (Found : C, 55·6; H, 3·9; N, 6·4. $C_{21}H_{16}O_8N_2S$ requires C, 55·2; H, 3·5; N, 6·1%). This material was also obtained from the corresponding sulphide (Apitzsch, *Ber.*, 1913, **46**, 3098) by oxidation with hydrogen peroxide in acetic acid solution.

The p-*nitrobenzyl* ester of m-carboxyphenyl-p-nitrobenzylsulphone (compare IX) was prepared by a similar process and formed plates, m. p. 203° (Found : C, 55·4; H, 4·1; S, 7·0. $C_{21}H_{16}O_8N_2S$ requires

*3-Keto-2-*p*-nitrophenyl-2 : 3-dihydrothionaphthen* 1 : 1-*Dioxide* (X R = $C_6H_4 \cdot NO_2$).—A solution of sodium (0·3 g.) in alcohol (75 c.c containing the sulphone ester (IX) (5 g.) was boiled for 2 hours. Th red sodium derivative which separated from the cooled liquid wa collected and treated with dilute sulphuric acid. The require *dioxide* was then obtained, after purification from acetic acid, i prisms, m. p. 186°. It was sparingly soluble in hot water, tl solution being yellow (Found: C, 55·3; H, 3·4. $C_{14}H_9O_5N$ requires C, 55·4; H, 3·0%).

3-Keto-2-carbethoxy-2 : 3-dihydrothionaphthen 1 : 1-*Dioxide* (X R = CO_2Et).—A solution of ethyl chloroacetate (13·5 g.) and potass ium *o*-sulphinobenzoate (14 g.) in alcohol (200 c.c.) and a little wate was boiled for 2 hours, the precipitated potassium chloride removed and a solution of sodium ethoxide (2·6 g.) added to the filtrate, whicl was then gently warmed. The yellow sodium derivative was col lected and decomposed with dilute sulphuric acid. From th solution obtained, ether extracted the required substance, whic was purified from alcohol and then found to be identical with th "anhydro"-compound of Feist (*loc. cit.*) (Found: C, 51·8; H, 4·0 Calc.: C, 51·9; H, 3·9%).

Hydroxy-derivatives of o-*Carboxydiphenyl Sulphide*.—A solutio of the dichloride (III) was prepared by the action of chlorine o *o*-thiolbenzoic acid suspended in carbon tetrachloride (7 c.c. fo every gram of the acid). After removal of free chlorine and hydroge chloride, the usual precautions for the exclusion of moisture bein taken, the solution was mixed with a phenol (2 mols.) in a suitabl volume of carbon tetrachloride or dry ether. The required materia had in most cases separated after 24 hours. The following product are typical of those obtained.

2-Carboxy-4'-hydroxydiphenyl sulphide (VI) formed small needle from acetic acid, m. p. 193° (Found: C, 63·3; H, 4·1; S, 12·8 $C_{13}H_{10}O_3S$ requires C, 63·4; H, 4·0; S, 13·0%). The structur assigned to the substance was shown by the conversion in warn sulphuric acid into 2-hydroxythioxanthone, the constitution o which has been determined by a method which will be subsequentl described.

2-Carboxy-2' : 4'-dihydroxydiphenyl sulphide,

$$C_6H_3(OH)_2 \cdot S \cdot C_6H_4 \cdot CO_2H,$$

prepared from resorcinol, separated from hot water in needles m. p. 190°, which assumed a yellow colour on exposure to ligh (Found: C, 59·7; H, 4·0; S, 12·1. $C_{13}H_{10}O_4S$ requires C, 59·5 H, 3·8; S, 12·2%).

The interaction of the dichloride and resorcinol in equimolecula proportion under the conditions described gave *bis-2'-carboxy*

phenylthiol-2 : 4-*dihydroxybenzene*, $C_6H_2(OH)_2(S{\cdot}C_6H_4{\cdot}CO_2H)_2$, which was obtained in small needles, m. p. 272°, soluble in hot alcohol and insoluble in water (Found : C, 57·9; H, 3·5. $C_{20}H_{14}O_6S_2$ requires C, 57·9; H, 3·3%).

o-Carboxyphenyl 2-hydroxy-α-naphthyl sulphide,

$$C_{10}H_6(OH){\cdot}S{\cdot}C_6H_4{\cdot}CO_2H,$$

prepared from β-naphthol, separated from alcohol in needles, m. p. 237°, which became yellow on exposure to light (Found : C, 68·9; H, 4·1. $C_{17}H_{12}O_3S$ requires C, 68·9; H, 4·0%).

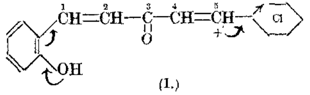
The yields of the *o*-carboxyphenyl sulphides obtained from the process are generally good and the method thus leads to a convenient synthesis of hydroxythioxanthones. Examples of this application will be described in a future communication.

KING'S COLLEGE, LONDON. [*Received, October* 10*th*, 1928.]

CCLXXIX.—*The Interaction of Ethyl Acetoacetate with Distyryl Ketones. Part IV. Selective Addition to Unsymmetrical Chlorodistyryl Ketones.*

By ISIDOR MORRIS HEILBRON and ROWLAND HILL.

IT was shown in Part III (Heilbron and Hill, J., 1927, 918) that when ethyl acetoacetate was condensed with *o*-hydroxychlorodistyryl ketones, the ester invariably attached itself to the ethenoid linkage adjacent to the *o*-hydroxyl, irrespective of the position of the chlorine atom in the opposing styryl residue. These results were unexpected, as in ketones of this type the double bond vicinal to the chlorine-containing styryl residue must, if direct addition occurs, be the more reactive owing to the development of a positive charge at C_5 (I) due to the capacity of the chlorine atom to act as an attractor for electrons.



(I.)

The addition of ethyl acetoacetate to the three isomeric *monochlorodistyryl ketones* and also to 2 : 3′-, 2 : 4′-, and 3 : 4′-*dichlorodistyryl ketones* has now been studied in the hope of arriving at some general idea of the effect of the position of the halogen atom upon the activation of the ethenoid linkages in a series of compounds free from the possible disturbing influence of an ortho-hydroxyl group.

The preparation of the monochlorodistyryl ketones was a matter

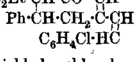
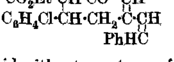
of considerable difficulty owing to the ease with which styryl meth ketone condensed with the chloroaldehydes, giving high-meltin amorphous polymerisation products in presence of alcoholic sodiu ethoxide. The desired results were ultimately attained by employin very low concentrations of alkali, as recorded in the following table

		Alkali concentration (NaOEt).				
Ketone.	Aldehyde.	1—3 mols.	0·5 mol.	0·1 mol.	0·02—0·03 mol.	0·01 mol
Methyl styryl ketone	*o*-Chlorobenzaldehyde	Amorphous solids	Oils	Oil	Ketone	Aldol
,,	*m*- ,,	,,	,,	,,	,,	Ketone
,,	*p*- ,,	,,	Ketone	Aldol	Aldol	Aldol

In all cases the aldols could be quantitatively converted into th distyryl ketones on treatment with boiling acetic anhydride.

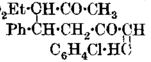
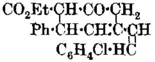
It was found impossible to obtain the dichlorodistyryl ketones b alkali condensations owing to the extraordinarily easy fission of th monochlorostyryl methyl ketones in presence of alkali. Fo instance, 2-chlorostyryl methyl ketone and *m*-chlorobenzaldehyd reacted in presence of 0·05 mol. of aqueous alkali, yielding, not th anticipated 2 : 3′-dichlorodistyryl ketone, but the symmetric 2 : 2′-dichloro-isomeride, a reaction obviously due to fission of th reacting monostyryl ketone (compare Heilbron and Buck, J., 192 **119**, 1500). The desired compounds were all obtained as crystalli halochromic salts by condensation in presence of dry hydroge chloride at 0°.

The addition of ethyl acetoacetate to the distyryl ketones offere no special difficulties when the reactants were condensed in presenc of alcoholic sodium ethoxide (0·1 mol.). The *cyclo*hexenones we readily obtained in crystalline form. Only one product was isolate in every case except 2-chlorodistyryl ketone, which gave tw *isomeric cyclohexenones* (m. p. 137° and 109°), $C_{23}H_{21}O_3Cl$. Thes two compounds had not resulted by addition of the ester to both th ethenoid linkages yielding *ethyl* 3-*phenyl*-5-o-*chlorostyryl*-Δ^5-cycl *hexen*-1-*one*-2-*carboxylate* (II) and ethyl 3-*o*-chlorophenyl-5-styry Δ^5-*cyclo*hexen-1-one-2-carboxylate (III), for on oxidation bot

(II.)   (III.)

isomerides yielded *o*-chlorobenzoic acid without any trace of benzo acid. The compounds may possibly be position isomerides. C these, the higher-melting *cyclo*hexenone has probably the formu ascribed (II), since treatment of *ethyl* (γ-*keto*-α-*phenyl*-ε-2-*chlor phenyl*-Δ^δ-*pentenyl*)*acetoacetate* (IV) with sodium ethoxide readi

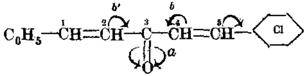
yields this product. On the other hand, the lower-melting isomeride, which is obtained only in poor yield, may be formed from the enolic form of (IV)—a reaction which is reminiscent of the coumalobenzopyran formation (Heilbron and Hill, *loc. cit.*); subsequent loss of water would then yield *ethyl 3-phenyl-5-*o*-chlorostyryl-*Δ^4-cyclo*hexen-1-one-2-carboxylate* (V). Alternatively, it is equally possible that the two compounds are stereoisomerides.

(IV.)   (V.)

None of the *cyclo*hexenones described in this communication produces the blood-red coloration with concentrated sulphuric acid originally observed by Borsche (*Annalen*, 1910, **375**, 145) and considered indicative of *cyclo*hexenones of this type.

The constitutions of the *cyclo*hexenones were determined by oxidation with potassium permanganate in acetone solution (Heilbron and Hill, *loc. cit.*). Each mono-substituted *cyclo*hexenone yielded the corresponding chlorobenzoic acid, and the fact was thus established that, irrespective of the position of the chlorine atom, the ethyl acetoacetate enters the molecule at the ethenoid linkage vicinal to the non-substituted benzene nucleus. Provided the initial reaction consists in the *direct* addition of the negative ester ion to the unsaturated centre, these results are again wholly at variance with the electronic conceptions of reactivity, which demand the formation of *cyclo*hexenones from which benzoic acid would be produced on oxidation.

It would thus seem that the mechanism of the reaction cannot consist in simple addition to a double bond. An alternative explanation, and one in harmony with the experimental results, can be found if the assumption is made that the activation of the ethenoid linkage is dependent upon the known tendency of the carbonyl oxygen atom to gain a negative charge. In such a case the following electronic conditions would obtain :



Process a is now the primary source of activation : process b, although secondary, is nevertheless essential. The latter effect must obviously be inhibited by the opposing general effect produced by the presence of the chlorine atom in the substituted styryl residue, a condition which does not apply to process *b′*. As a consequence, the addition of the ester would inevitably affect the ethenoid linkage of

the unsubstituted styryl residue, as carbon atom C¹ now forms the terminal atom of the true "crotonoid" system (compare Allan, Oxford, Robinson, and Smith, J., 1926, 403).

The question of the addition to the dichlorodistyryl ketones is a complex one. Here the inhibitions of phases *b* and *b'* due to the strong general effect of the halogen atoms must become very nearly equal. Consequently, the negative ester ion will attach itself to either C¹ or C⁵ according as the one or the other is more strongly influenced by the position of the chlorine atom in the respective aromatic nuclei. The actual effect is well illustrated in the case of the chlorobenzoic acids, where the order is $o > m > p$ as shown by their dissociation constants ($K = 0{\cdot}132$, 0·0155, and 0·0093, respectively). Exactly similar relationships apply to the *cyclo*hexenones. For instance, 2 : 3'-dichlorodistyryl ketone forms *ethyl 3-*o*-chlorophenyl-5-*m*-chlorostyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylate*, from which *m*-chlorobenzoic acid is produced on oxidation. Similarly, the *cyclo*hexenones formed from both 2 : 4'- and 3 : 4'-dichlorodistyryl ketones yield *p*-chlorobenzoic acid.

EXPERIMENTAL.

2-Chloro-β-hydroxy-β-phenylethyl Styryl Ketone.—A solution of styryl methyl ketone (20 g.) and *o*-chlorobenzaldehyde (19 g.) in alcohol (150 c.c.) and water (100 c.c.) was treated with aqueous sodium hydroxide (5·5 c.c. of 1%; 0·01 mol.) and kept at 0° for several days. The yellow oil obtained, which solidified on vigorous scratching, formed long, colourless needles, m. p. 79—80° (yield, 11 g.), after repeated crystallisation from absolute alcohol. By liberally seeding the reaction mixture with the aldol as soon as the condensate commenced to separate, the yield was increased to 31 g. (Found: C, 71·4; H, 5·3. $C_{17}H_{15}O_2Cl$ requires C, 71·2; H, 5·3%).

2-Chlorodistyryl ketone may be prepared directly as described above by increasing the alkali concentration to 0·03 mol. (16·5 c.c. of a 1% solution). The separated pale yellow oil gradually formed a semi-solid mass (10 days), from which the aqueous layer was decanted. The residue was taken up in ether and, after removal of solvent from the dried extract, yellow crystals were obtained mixed with a viscous oil, which was removed by extraction with a small quantity of alcohol. The solid residue was crystallised repeatedly from absolute alcohol, from which the pure *ketone* separated in short yellow needles, m. p. 82—83°. Alternatively, the ketone can readily be prepared by refluxing the aldol for 2 hours with acetic anhydride (Found: C, 76·2; H, 5·1. $C_{17}H_{13}OCl$ requires C, 76·0; H, 4·9%).

3-*Chlorodistyryl ketone*, prepared in an exactly similar manner to the 2-chloro-isomeride, separated from alcohol in large plates, m. p. 108—109° (Found: C, 75·6; H, 4·8%).

4-*Chloro-β-hydroxy-β-phenylethyl Styryl Ketone*.—A solution of styryl methyl ketone (8 g.) and *p*-chlorobenzaldehyde (7·5 g.) in alcohol (80 c.c.) and water (60 c.c.) was treated with aqueous sodium hydroxide (8 c.c. of 1%) at room temperature. The yellow oil obtained, which solidified, was crystallised first from alcohol and finally from benzene, from which the *aldol* separated in colourless needles, m. p. 108—109° (Found: C, 71·2; H, 5·3%). On treatment of the aldol with acetic anhydride in the usual way, an excellent yield of 4-chlorodistyryl ketone was obtained, which crystallised from alcohol in glistening, pale yellow leaflets, m. p. 134°. The distyryl ketone may also be prepared directly from its constituents *if the concentration of the alkali be increased to 0·5 mol.* This substance has previously been obtained by Straus and Blankenhorn (*Annalen*, 1917, **415**, 256), but working under their *conditions*, we have only succeeded in isolating the aldol.

2 : 3'-*Dichlorodistyryl Ketone*.—2-Chlorostyryl methyl ketone (20 g.), prepared by Vorländer's method (*Annalen*, 1897, **294**, 291), and *m*-chlorobenzaldehyde (15·8 g.) were dissolved in dry ether (60 c.c.) and saturated with dry hydrogen chloride at 0°; heat was developed and the solution rapidly assumed a deep purple colour. After the mixture had been kept for 3 days in the ice-chest, the crystalline, red, halochromic salt was collected, washed with dry ether, and dissolved in boiling alcohol. The solution was then treated with sufficient sodium carbonate solution to discharge the red colour. After removal of precipitated inorganic matter, the yellow filtrate was diluted with water, and the precipitated *distyryl ketone* recrystallised from aqueous alcohol. It formed long yellow needles, m. p. 67—68°, sparingly soluble in light petroleum, ether, and carbon disulphide (Found: C, 67·1; H, 3·7. $C_{17}H_{12}OCl_2$ *requires* C, 67·3; H, 3·9%).

2 : 4'-*Dichlorodistyryl ketone* was prepared in a similar manner. It crystallised from alcohol in yellow needles, m. p. 109° (Fonnd: C, 67·5; H, 4·0%).

3-*Chlorostyryl Methyl Ketone*.—A solution of *m*-chlorobenzaldehyde (20 g.) in acetone (100 g.) was diluted with water to 2000 c.c. and then treated with aqueous sodium hydroxide (100 c.c. of 10%). The mixture was mechanically shaken for 48 hours, the separated oil extracted with ether, and the solution dried. After removal of solvent, the residual oil was distilled; the portion, b. p. 171°/20 mm., slowly crystallised at room temperature, forming yellow plates, m. p. 28—29° (yield, 17 g.). The *ketone* is readily soluble in the

usual organic solvents, but may be crystallised from light petroleum (Found : C, 66·1 ; H, 5·0. $C_{10}H_9OCl$ requires C, 66·5 ; H, 5·0%).

3 : 4′-*Dichlorodistyryl ketone*, prepared by condensation of the above ketone with *p*-chlorobenzaldehyde by means of dry hydrogen chloride, separated from alcohol in pale yellow plates, m. p. 134° (Found : C, 67·4 ; H, 3·9%).

Ethyl (γ-*Keto*-α-*phenyl*-ε-2-*chlorophenyl*-Δ[δ]-*pentenyl*)*acetoacetate* (IV).—2-Chlorodistyryl ketone (2·5 g.) and ethyl acetoacetate (8 c.c.) were heated under reflux on the water-bath for 48 hours in presence of piperidine (12 drops). Treatment of the reaction mixture with aqueous alcohol produced a dark brown oil, which solidified. The crude *ketone*, repeatedly crystallised from absolute alcohol in presence of animal charcoal, formed colourless needles, m. p. 112°, which dissolved in concentrated sulphuric acid to an orange solution (*Found : C, 69·5 ; H, 5·9. $C_{23}H_{23}O_4Cl$ requires C, 69·3 ; H, 5·8%*).

Ethyl 3-*phenyl*-5-o-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate* (II) is readily obtained by gently warming the previous compound with alcoholic sodium ethoxide. It is more suitably prepared by the following direct method : 2-Chlorodistyryl ketone (20 g.), dissolved in a mixture of hot absolute alcohol (80 c.c.) and ethyl acetoacetate (12 g.), was heated for 15 minutes on a water-bath with alcoholic sodium ethoxide (18 c.c. of a 1% solution); the colour of the solution changed from yellow to orange and, on cooling, yellow crystals were slowly deposited. These were collected after 2 days and crystallised from dilute alcohol; the cyclo*hexenone* was then obtained in colourless feathery needles, m. p. 137°, sparingly soluble in cold alcohol and light petroleum, very soluble in chloroform and glacial acetic acid (yield, 10·5 g.). The solution in concentrated sulphuric acid is orange (Found : C, 72·2 ; H, 5·6. $C_{23}H_{21}O_3Cl$ requires C, 72·5 ; H, 5·5%).

Oxidation. The *cyclo*hexenone was dissolved in acetone and treated at room temperature with finely powdered potassium permanganate, added in small quantities at a time and in very slight excess. The solid residue was finely powdered and repeatedly extracted with boiling water, and the solution rendered acid. The colourless needles which were deposited on cooling were repeatedly crystallised from boiling water, and the product, m. p. 138—139°, was identified as *o*-chlorobenzoic acid (no depression of m. p. in admixture with an authentic specimen, m. p. 142°).

3-*Phenyl*-5-o-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*.—A solution of the preceding ester (3 g.) in glacial acetic acid (50 c.c.) was refluxed for 1 hour with sulphuric acid (30 c.c. of 40%). The crude solid which separated on dilution of the reaction mixture crystallised from

alcohol in yellow plates, m. p. 142° (Found : C, 77·8 ; H, 5·2. $C_{20}H_{17}OCl$ requires C, 77·8 ; H, 5·5%).

*Ethyl 3-Phenyl-5-*o*-chlorostyryl-*Δ^4-cyclo*hexen-1-one-2-carboxylate*(?) (V).—The filtrate of the reaction mixture from which the crude Δ^5-*cyclo*hexenone ester had been separated yielded, after concentration and dilution with water, a viscous yellow oil which very slowly solidified in the ice-chest. The crude product separated from ethyl alcohol in colourless plates (3 g.), m. p. 107° (Found : C, 72·6 ; H, 5·5%). This isomeride dissolves in concentrated sulphuric acid to an orange solution and is more soluble in the usual solvents than the higher-melting Δ^5-compound. On oxidation, *o*-chlorobenzoic acid was isolated, but no trace of benzoic acid.

3-*Phenyl-5-*o*-chlorostyryl-*Δ^4-cyclo*hexen-1-one* (?) was prepared by a similar method to that employed for the preparation of the Δ^5-isomeride. It crystallised from absolute alcohol (blood-charcoal) in golden-yellow needles, m. p. 136—137°. A mixed melting point with 3-phenyl-5-*o*-chlorostyryl-Δ^5-*cyclo*hexen-1-one (m. p. 142°) produced a depression of more than 25° (Found : C, 77·4 ; H, 5·8%).

*Ethyl 3-phenyl-5-*m*-chlorostyryl-*Δ^5-cyclo*hexen-1-one-2-carboxylate* was prepared by the interaction of 3-chlorodistyryl ketone and ethyl acetoacetate by a similar method to that previously described. It separated from the diluted reaction mixture as a mobile yellow oil which slowly solidified. The pure cyclo*hexenone* was obtained by repeated crystallisation from methyl alcohol and formed yellow prisms, m. p. 105—106° (Found : C, 72·2 ; H, 5·4%). Oxidation with potassium permanganate yielded *m*-chlorobenzoic acid, m. p. 148—149°.

*Ethyl 3-phenyl-5-*p*-chlorostyryl-*Δ^5-cyclo*hexen-1-one-2-carboxylate*, prepared from 4-chlorodistyryl ketone, was obtained, after repeated crystallisation from alcohol, in prisms, m. p. 124—125° (Found : C, 72·2 ; H, 5·5%). The acid (m. p. 236°) produced on oxidation was identified as *p*-chlorobenzoic acid by comparison with an authentic specimen.

*Ethyl 3-*o*-chlorophenyl-5-*m*-chlorostyryl-*Δ^5-cyclo*hexen-1-one-2-carboxylate* separated from methyl alcohol in pale yellow needles, m. p. 108—109° (Found : C, 66·7 ; H, 4·8. $C_{23}H_{20}O_3Cl_2$ requires C, 66·5 ; H, 4·8%). It is sparingly soluble in light petroleum, carbon disulphide, and cold methyl alcohol, readily soluble in chloroform, acetone, and ethyl acetate. Oxidation under the usual conditions gave *m*-chlorobenzoic acid, m. p. 149—150°.

*Ethyl 3-*o*-chlorophenyl-5-*p*-chlorostyryl-*Δ^5-cyclo*hexen-1-one-2-carboxylate* crystallised from alcohol in slender yellow needles, m. p. 142° (Found : C, 66·3 ; H, 4·8%) and gave *p*-chlorobenzoic acid on

Ethyl 3-m-*Chlorophenyl*-5-p-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*.—3 : 4′-Dichlorodistyryl ketone (8 g.), dissolved in a minimum quantity of absolute alcohol (200 c.c.), and ethyl acetoacetate (5 g.) were refluxed for 15 minutes with sodium ethoxide (7·2 c.c. of a 1% solution). After concentration of the reaction mixture, yellow crystals were gradually deposited which were recrystallised from absolute alcohol. The purified cyclo*hexenone* separated in yellow prisms (6 g.), m. p. 122° (Found : C, 66·2; H, 5·1%), which dissolved in concentrated sulphuric acid to an orange-red solution. It is sparingly soluble in cold alcohol and carbon disulphide, readily soluble in acetone, benzene, and ethyl acetate. Oxidation gave *p*-chlorobenzoic acid, m. p. 236—238°, which was identified in the usual manner.

2 : 2′-*Dichlorodistyryl Ketone*.—2-Chlorostyryl methyl ketone (9 g.) and *m*-chlorobenzaldehyde (7 g.) were dissolved in alcohol (60 c.c.) and the solution was rendered just turbid by dilution with water. Aqueous sodium hydroxide (10 c.c. of a 1% solution) was added with vigorous shaking. The mobile yellow oil that separated was removed by extraction with ether and dried over anhydrous sodium sulphate. The oily residue left after removal of solvent was dissolved in ethyl acetate; crystals were then slowly deposited. The crude substance was recrystallised first from alcohol and finally from ethyl acetate, giving yellow needles, m. p. 124° (Found : C, 67·0; H, 4·1%), which were identified as 2 : 2′-dichlorodistyryl ketone by comparison with a specimen of the ketone prepared in the usual manner.

THE UNIVERSITY, LIVERPOOL. [*Received, August* 31*st*, 1928.]

CCCLXXX.—*The Heat of Adsorption of Oxygen on Charcoal. Part III.*

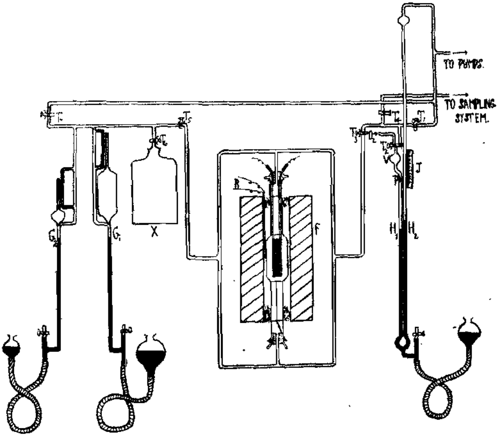
By DOUGLAS MCKIE.

ATTEMPTS are now described to refine the method of Blench and Garner (Part I; J., 1924, **125**, 1288) for determining the heat of adsorption of oxygen on charcoal under various conditions of temperature and pressure, and to extend it to the general case of the measurement of the heat of adsorption of a gas on a solid surface. So far, only one case, *viz.*, that of the adsorption of oxygen on charcoal, has been studied. The results obtained have already been summarised and their theoretical implications discussed in Part II (Garner and McKie, J., 1927, 2451).

Component Parts of Apparatus.—*Reaction vessel.* The reaction vessel is shown on a large scale in Fig. 2; it consisted of a tube of

fused quartz, 40 cm. long and 2 cm. in diameter, open at both ends, the middle section being blown out in the form of a cylindrical bulb, A, 10 cm. long and 4·5 cm. in diameter. Hollow, closed stoppers, S_1 and S_2, of "Durosil" glass were ground to fit the open ends. *A continuous and rapid current of cold water was* passed through each stopper *via* the tubes, D D, to prevent undue heating of the rubber grease used to keep the ground joints vacuum-tight. The stoppers were further protected from the heat radiated along the tube of the furnace by means of fused quartz plates, R R,

Fig. 1.

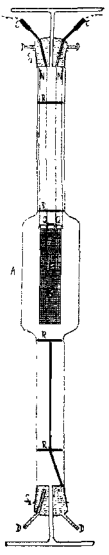


arranged inside the vessel, two being placed on each side of the bulb, one just level with the shoulders of the latter and the other on a level with the end of the furnace. The upper two were attached to the wires carrying the container, K. The lower pair were joined as shown, one being fused to each end of a suitable length of quartz rod, and were supported on the lower stopper by a short limb of quartz, fused obliquely to the lower plate so as to rest clear of the tube passing through the stopper.

A tube was sealed through each stopper for the admission of gas, thus ensuring even distribution to each end of the mass of

charcoal in K. Through the upper stopper there were also sealed two tubes for carrying the wires of the thermocouple, E, each wire being sealed into its tube at a distance of about 3 cm. from the stopper. In the fusion of the glass around the metal, the wires became brittle at this point, where there was always a tendency for them to be bent, and in order to prevent this bending, glass cups, C C, were fused on to the tubes carrying the wires. After the wires had been sealed into the leads just below the cups, the latter were filled with molten wax, which on solidification prevented any movement of the wires near the glass–metal joints.

FIG. 2.



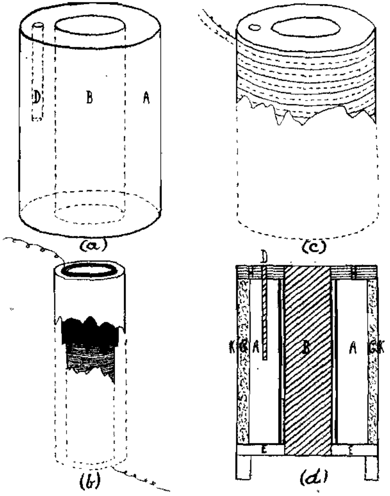
The charcoal, about 5—6 g., was supported in the container, K, of 200-mesh platinum gauze, suspended by platinum wires from the glass hooks, N N, fused to the base of the stopper, S_1. The top of the container was closed by a platinum lid, bearing an insulating H-tube, Q Q, of fused quartz, carrying the wires of the thermocouple.

Furnace. The ordinary laboratory pattern of electrical furnace provided sufficient lagging for the reaction vessel to keep it at constant temperature during determinations at room temperature; in the experiments at higher temperatures, however, this furnace was not suitable, as its temperature could not be maintained sufficiently constant owing to variations in the voltage of the mains, and the furnace F was therefore designed. It consisted of a copper cylinder, A (Fig. 3*a*), about 27 kg. in weight, 25 cm. in length, and 15 cm. in diameter, cast with a central cylindrical bore, B, of 7·5 cm. diameter, which carried two concentric cylindrical quartz tubes of the same length as A. The inner of these had an internal diameter of 5 cm. and walls 0·1 cm. thick. Along its whole length, a coil of nichrome wire (20 S.W.G.) was closely wound and securely fastened at the ends. This tube was placed inside the outer tube, of external diameter 7·5 cm. and wall thickness 0·7 cm., and cemented into position by packing the annular space with alundum cement. The whole arrangement, shown in Fig. 3(*b*), was then passed into the bore of the copper cylinder, a thin layer of asbestos paper being placed between the copper and the quartz. The ends of the coil were connected *via* an adjustable series resistance with the 220-volt main. This coil was used to maintain the reaction vessel at 950° during the activation of

the charcoal. The reason for its special construction appears below.

The copper cylinder was wound on the outside with two subsidiary coils of nichrome ribbon, 0·1588 cm. by 0·0127 cm., each passing along its whole length, as shown in Fig. 3(c), and each having a resistance of about 45 ohms. Insulation between the copper and the coils was provided by a layer of asbestos paper.

FIG. 3.



The copper cylinder, etc., was then mounted on a fire-brick, E, 2·5 cm. high, in which a hole had been drilled of diameter equal to that of the bore of A, and placed in a rectangular tin, K, of cross-section 20 cm. by 20 cm. and height 30 cm., as shown in Fig. 3(*d*). The hollow portion, G, was packed with asbestos wool; H consists of asbestos boards with circular holes to correspond to the bores at the top of A.

The subsidiary heating coils were used during the determination of heats of adsorption at temperatures above atmospheric. By

means of them, the copper cylinder was heated to the temperature of experiment, both coils carrying current and being separately connected *via* adjustable series resistances with the 220-volt main. The temperature of the cylinder was controlled by means of a mercury-in-glass (hard) regulator, the bulb of which was placed in the hole, D, drilled in the copper, as shown in Fig. 3(*a*) and (*d*). This hole was 1·25 cm. in diameter and 12·5 cm. long, and the bulb of the regulator was constructed so as to fill it as exactly as possible. The regulator operated an electromagnetic relay, so arranged as to " break " the current through one of the subsidiary coils, if and when the temperature of the copper exceeded that desired. Thermal contact between the copper and the glass bulb of the regulator was improved by an intermediate film of B.P. paraffin. This system of regulation maintained the temperature constant to within $\pm$ 0·05° at 100° and $\pm$ 0·10° at 200°.

The purpose of the several coils will now be clear. The main coil was designed to carry 10 amps. and thus to provide rapid heating of the reaction vessel to the temperature of activation. The subsidiary coils carried currents of $\frac{1}{2}$—$1\frac{1}{2}$ amps. Such currents gave small fluctuations of temperature in a furnace of so large a thermal capacity. The smaller current was always less than 1 amp., and was therefore such as to be easily broken by the relay. These subsidiary coils could not be used for activation at high temperature : heating was too slow, and the coils wore out under such drastic usage. Further, if the copper was heated to 950°, considerable oxidation occurred; hence the main coil was introduced for the preliminary activation. The lagging effect produced by the thick, outer, quartz tube was such that the temperature of the copper never rose beyond 600—700° during the two hours when the reaction vessel was at 950°, and oxidation was so slight that after months of use scaling was inappreciable. Further, the temperature of the reaction vessel could be raised from 18° to 950° in 10 minutes.

Pumping system. The pumping system consisted of a second-stage mercury-vapour diffusion pump, working under the backing pressure set up by a " Hyvac " rotary oil pump.

Sampling system. The sampling system consisted of a second-stage mercury-vapour diffusion pump in series with a Töpler pump, which allowed of the collection of a sample of gas from the reaction vessel after adsorption had taken place. The sample was collected in a capillary tube, where it was analysed as described below.

Gas burette. The gas burette, V (Fig. 1), was the one described in Part I (p. 1291), and the same procedure was followed.

Method of Recording Increments of Temperature.—Changes of temperature produced by adsorption were recorded by means of a

platinum–platinum-rhodium thermocouple, of which the " hot " junction, E, was embedded in the charcoal as shown in Fig. 2, the " cold " junction being maintained at a constant temperature (that of the furnace tube) either by insertion in a Dewar vessel containing water at room temperature in the experiments at that temperature, or by being placed inside the tube of the furnace close to the bulb of the reaction vessel in the experiments at higher temperatures. The thermocouple system was connected in series with a rigidly mounted Moll galvanometer, the mirror of which was illuminated by a 100 c.p. " Pointolite " lamp, enclosed in a light-tight box, and so arranged that an image of a slit as a fine vertical line of light was reflected from the mirror on to the cylindrical lens of a clock-work camera. This lens focussed the line to a point image, the movements of which were recorded on bromide paper, wound on a moving drum.

Calibration of Thermocouple.—The thermocouple was calibrated at 0° by means of two Dewar vessels, one containing crushed ice and water, and the other water at 3—4°. Calibration at 15° was carried out in the same manner by means of two samples of water at different temperatures near 15°. Similar calibrations were made at 60°, 100°, and 190° by means of a pair of baths at constant neighbouring temperatures. All temperatures were read on standard thermometers. The differential deflexions per degree were then plotted against the corresponding temperatures, and a smooth curve was drawn through the points obtained. From this the deflexion per degree difference of temperature could be read at any desired temperature.

Correction for the " Gas Effect."—The temperature–time curves obtained on the photographs were corrected for loss of heat by radiation as described later, but a further correction was necessary in the case of determinations at temperatures above atmospheric. This was due to the " gas effect," which has already been described in detail (Part I, pp. 1291—1292)—briefly, it is that rise of temperature which occurs on admission of any gas, whether adsorbed or inert, to the hot, evacuated reaction vessel. The phenomenon is largely due to the gradient of temperature inside the vessel between the walls of the latter and the thermocouple, this gradient being caused by convection currents in the reaction vessel. At very low pressures, heat is conducted away to the ends of the vessel by convection more rapidly than it is conducted inwards to E from the walls of A (Fig. 2).

This effect was allowed for as follows. Argon, purified as described later, was admitted to the reaction vessel from the gas burette in such amount that it gave in that vessel a pressure approximately

equal to that which obtained there after the adsorption of oxygen in the experiment to which the correction was to be applied. The rise of temperature occurring on admission of argon, *i.e.*, the " gas effect," was measured photographically as in the method previously described. The experiments showed that the temperature rose slowly, taking several minutes to attain its maximum, and then remained at a steady level, say, x units higher than the original temperature. It could be restored to that value only if and when the argon was removed by evacuation. The actual increment of temperature due to adsorption of oxygen was therefore taken to be the difference between x and the rise of temperature occurring when adsorption of oxygen took place. Similar experiments with argon were made at the various pressures and temperatures at which experiments with oxygen took place, and the corrections thus determined were applied to their respective experiments.

Complete Apparatus.—The assembled apparatus is shown in Fig. 1. On one side the reaction vessel was connected *via* tap T_5 with the bottle X (see below), and thence with the McLeod gauges, G_1 and G_2, which in turn were connected with the pumping system by means of the tap T_7; and on the other side it was connected with the pumping system *via* tap T_1. A further tap, T_3, was inserted between tap T_1 and the reaction vessel. Tap T_2 connected the reaction vessel with the gas burette. At a suitable point the sampling system was connected to the main apparatus by way of tap T_4. Save for the stoppers S_1 and S_2, the glass parts of the apparatus were of soft glass. Junction between the soft- and hard-glass parts of the apparatus was effected through ground joints, not shown in the diagrams.

Volume of the Apparatus.—The volume of the apparatus was determined by admitting a measured amount of oxygen from the gas burette to that part of the evacuated apparatus between taps T_1, T_4, and T_7, measuring the resulting pressure on the McLeod gauges, and then applying Boyle's law. The value obtained applied only to determinations at room temperature, because in the other experiments the reaction vessel was at a higher temperature, and the consequent thermal expansion of the gas led to an apparent decrease in the volume of the apparatus. To allow for this, the " apparent " or " equivalent " volume of the apparatus (see Part I, pp. 1291—1292) was determined by the method just described with the reaction vessel at various temperatures, carbon being absent.

Materials.—Oxygen was obtained by heating pure potassium permanganate and was dried by passage through phosphoric oxide.

The charcoal consisted of those particles of the vegetable charcoal, " Norit," which were sieved by the 100- and screened by the

150-mesh sieve. This portion was repeatedly boiled with hydrochloric and hydrofluoric acids to remove lime and silica, the ash content being thereby reduced from 7% to 0·3% and all traces of lime removed.

The argon was obtained from a sample containing about 5% of nitrogen and traces of oxygen and of the rare gases. For our purposes, this last impurity could be ignored. Nitrogen was removed by a modified form of the method of Rayleigh and Ramsay (*Phil. Trans.*, 1895, *A*, **186**, 197), the confining liquid being mercury instead of weak alkali. The author's thanks are due to Dr. M. W. Travers, F.R.S., who very kindly constructed the necessary apparatus, directed him in the technique of the process, and purified a large sample of the argon used. The nitrous gases formed were absorbed by a layer of aqueous caustic soda solution floating on the mercury. Excess of oxygen was subsequently removed by ignited phosphorus. Possible traces of phosphorus vapour were then condensed by cooling with solid carbon dioxide and alcohol. As a test of its purity, 1 c.c. (N.T.P.) of the argon was admitted at room temperature to 5 g. of charcoal previously activated at 950° in the usual manner. No measurable rise of temperature occurred, and the residual pressure indicated that only a negligible trace, if any, of the argon could have been adsorbed.

Method of Experiment.

This can best be followed by reference to Fig. 1. About 5—6 g. of the purified charcoal were heated in the reaction vessel by means of the furnace, F, for 2 hours at 950° under the high vacuum set up by the pumping system. During this time, the vacuum progressively improved to a steady value of 0·002 cm., below which it could not be reduced while the high temperature was maintained. The temperature of the furnace during this activation was recorded by means of a platinum–platinum-rhodium thermocouple, B, operating a sensitive millivoltmeter, giving direct readings of temperature. At the end of the 2 hours, the current through the furnace was cut off, but pumping was continued. As the temperature fell, the vacuum improved, and at 650° it was 1×10^{-4} mm. All taps, except T_6, were then closed.

When the furnace had cooled to the temperature of the experiment, suitable currents were passed through the subsidiary heating coils, and the thermoregulator was adjusted to give the temperature desired. When constancy of temperature had been obtained, or, if the experiment was at room temperature, when the furnace had cooled to that temperature, a measured amount of oxygen was admitted from the burette through tap T_3 to that section of the

leading tubes between taps T_1, T_3, and T_4, and confined there by closing tap T_2. The shutter of the camera was then opened, and one minute later the gas was admitted to the reaction vessel by opening tap T_3. After the lapse of another minute (test experiments having shown the maximum temperature to be reached within this time), tap T_5 was opened for 10 seconds for removal of a sample of the residual gas to that part of the apparatus between taps T_5 and T_7. The pressure of this gas was then read on the McLeod gauges. As indicated above, tap T_6 was open during this sampling; this tap connected the apparatus with the large bottle, X (of about 2½ litres capacity), which was incorporated in the apparatus to remove from the reaction vessel as much as possible of the gas remaining after adsorption, preliminary experiments having shown that the initial rapid process of adsorption was followed by a much slower one, in which the oxygen was gradually taken up over a period of several days. This immediate removal of the bulk of the residual gas greatly reduced the pressure in the reaction vessel, and therefore either arrested further adsorption after the maximum temperature had been reached or reduced it to negligible proportions, thereby giving the true cooling curve and so permitting accurate correction for loss of heat by radiation.

When the temperature of the charcoal had fallen to its original value, the shutter of the camera was closed and the photographic record developed. At the same time taps T_4 and T_5 were opened, and the residual gas was removed by means of the Töpler pump for analysis. The apparatus was then evacuated to a pressure of 1×10^{-4} mm. without raising the temperature, after which a second admission of oxygen was made, and sometimes a third. After the last admission the charcoal was reactivated at 950° as before.

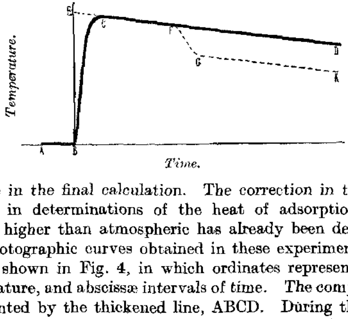
The sample of residual gas, collected *via* the Töpler pump in a capillary tube, was tested for carbon dioxide with an aqueous solution of caustic soda, for oxygen with alkaline pyrogallol, and for carbon monoxide with ammoniacal cuprous chloride. The various contractions were measured in the usual manner and the composition of the gas was calculated therefrom.

In the removal of the bulk of the residual gas to the bottle X and the McLeod gauges, the tap T_5 was opened for 10 seconds only. This interval of time was insufficient for the attainment of equal pressure throughout the apparatus, and therefore calibrations were made to find what equilibrium pressure corresponded to the pressure recorded by the gauges. The charcoal was removed from the apparatus, which was then evacuated to a pressure of 1×10^{-4} mm., after which taps T_1, T_4, T_5, and T_7 were closed. A measured sample of oxygen was admitted from the gas burette, and the same

procedure followed as in an actual experiment. After the pressure of the sample had been measured on the McLeod gauges, tap T_5 was opened. When equilibrium had been attained throughout the apparatus, the pressure was again read on the McLeod gauges. Varying amounts of oxygen were admitted in this manner so as to obtain figures covering the range of pressure of the experiments carried out. Values of the equilibrium pressure were then plotted against corresponding values of the observed pressure, and a smooth curve was drawn through the points obtained. From this curve the pressure corresponding to any observed pressure could be read, and from this value and the known volume of the apparatus the volume of gas unadsorbed was then calculated.

The volume of oxygen adsorbed by the charcoal was obtained by taking the difference between the volume admitted and that unadsorbed. Reduction of this volume to standard temperature

FIG. 4.



was made in the final calculation. The correction in the volume necessary in determinations of the heat of adsorption at temperatures higher than atmospheric has already been described.

The photographic curves obtained in these experiments were of the form shown in Fig. 4, in which ordinates represent intervals of temperature, and abscissæ intervals of time. The complete curve is represented by the thickened line, ABCD. During the interval of time from B to C, *i.e.*, the time taken to attain the maximum temperature, heat was being lost by the system through radiation, and to correct for this loss the line CD was produced backwards to cut the axis of temperature in the point E. The interval of temperature represented by BE was then taken to be the increment due to adsorption.

In the calculation of the heat evolved, this increment was multiplied by the thermal capacity of the materials undergoing that increment, *viz.*, the charcoal and the platinum container. The specific heats of platinum from 0° to 200° have been given by Mills (*J. Physical Chem.*, 1917, **21**, 345), who has also given similar data

for graphite. As Weber (*Pogg. Ann.*, 1875, **154**, 557) has shown that the specific heat of wood charcoal over the range 0—225° exceeds that of graphite by the constant amount 0·003, the following values were used in calculating thermal capacities :

	Specific heat (g.-cals.).		
Temp.	Platinum.	Graphite.	Wood-charcoal.
0°	0·0310	0·156	0·159
50	0·0318	0·195	0·198
100	0·0323	0·233	0·236
200	0·0332	0·298	0·301

The heat due to the adsorption of oxygen, *i.e.*, the difference between the total heat liberated and that due to the production of oxides of carbon (determined from the analyses of gaseous products), was expressed as kg.-cals. per g.-mol. of oxygen adsorbed, the oxygen being corrected to standard temperature. No correction was necessary for deviations from Boyle's law.

In the experiments at temperatures above that of the room, correction was made for the "gas effect" by the method already described.

Results.

Heat of Adsorption of Oxygen on Charcoal at Room Temperature.—In Table I are the values obtained for the heat of adsorption of oxygen on charcoal at room temperature after activation at various temperatures from 750° to 950°, approximately the same amount of oxygen, about 1·5 c.c. (N.T.P.), being admitted in every case.

TABLE I.

Heats of Adsorption of Oxygen on Charcoal at Room Temperature after Activation at Different Temperatures.

Expt.	Temp. of activation.	Temp. of expt.	Oxygen admitted, c.c.	Pressure of sample (mm.), obs.	corr.	Oxygen adsorbed, c.c.	Rise of temp.	Heat evolved, g.-cals.	Heat of adsorption, Cals./mol.
1	950°	20°	1·545	0·026	0·051	1·303	2·89°	3·61	67
2	950	20	1·620	0·035	0·062	1·325	2·93	3·66	66
3	900	19·5	1·556	0·053	0·086	1·147	2·59	3·24	68
4	950	20	1·556	0·040	0·069	1·228	2·89	3·61	71
5	950	20·5	1·549	0·047	0·079	1·174	2·78	3·50	72
6	850	20	1·542	0·094	0·134	0·905	2·11	2·64	70
7	800	21·5	1·535	0·130	0·174	0·709	1·59	2·00	68
8	800	22	1·478	0·077	0·117	0·922	2·19	2·76	72
9	750	21	1·556	0·142	0·186	0·672	1·59	2·00	72
10	950	21	1·474	0·047	0·079	1·099	2·52	3·18	70
11	800	20·5	1·492	0·110	0·153	0·765	1·78	2·24	70

Mean molar heat of adsorption = 70 Cals.

Note.—The experiments were carried out in the order shown, *i.e.*, with intermediate activations at 950° to ascertain whether any decay in the activity of the charcoal had occurred. Mass of charcoal = 5·96 g. Mass of platinum = 6·605 g. All volumes are referred to normal pressure and room temperature.

Table II.

Heats of Adsorption of Oxygen on Charcoal at Room Temperature after Activation at 950°.

Expt.	Temp. of expt.	Adm. i, ii, or iii.	Oxygen admitted, c.c.	Pressure of sample (mm.), obs.	Pressure of sample (mm.), corr.	Oxygen adsorbed, c.c.	Rise of temp.	Heat evolved, g.-cals.	Heat of adsorption, Cals./mol.
			Volume of oxygen admitted = 0·5 c.c. (approx.).						
12	20·5°	i	0·639	0·006	0·016	0·563	1·17°	1·39	59
13	21	ii	0·604	0·010	0·024	0·490	0·93	1·11	55
14	20·5	i	0·586	0·001	0·004	0·567	1·21	1·44	61
15	15	i	0·519	0·003	0·008	0·481	1·07	1·24	61
16	15	ii	0·533	0·033	0·059	0·253	0·50	0·58	54
17	15	iii	0·526	0·047	0·078	0·155	0·18	0·21	32
			Volume of oxygen admitted = 1·0 c.c. (approx.).						
18	21	i	1·172	0·032	0·059	0·892	1·90	2·26	61
19	21·5	ii	1·137	0·051	0·083	0·743	1·45	1·73	56
20	22·5	iii	1·119	0·114	0·157	0·373	0·52	0·62	40
21	18	i	1·098	0·005	0·013	1·036	2·24	2·64	61
22	18	i	1·119	0·007	0·017	1·038	2·31	2·73	63
23	18·5	ii	1·084	0·077	0·117	0·528	0·93	1·10	50
24	17	i	1·006	0·008	0·019	0·916	2·11	2·47	64
25	21	i	1·119	0·004	0·013	1·057	2·21	2·63	60
			Volume of oxygen admitted = 1·5 c.c. (approx.).						
26	18	i	1·563	0·014	0·033	1·406	3·45	4·07	69
27	18	i	1·510	0·024	0·048	1·282	3·17	3·74	70
28	19	ii	1·545	0·118	0·161	0·780	1·72	2·03	62
29	19	i	1·517	0·027	0·051	1·275	3·07	3·62	68
30	19	ii	1·482	0·086	0·126	0·892	1·90	2·24	60
31	19	iii	1·492	0·179	0·224	0·428	0·62	0·73	41
32	19	i	1·553	0·027	0·052	1·306	3·31	3·91	72
33	19·5	ii	1·545	0·147	0·191	0·638	1·41	1·66	62
34	20	i	1·531	0·020	0·042	1·331	3·34	3·94	71
35	20·5	ii	1·563	0·150	0·194	0·641	1·38	1·64	62
36	19·5	i	1·538	0·020	0·042	1·338	3·21	3·79	68
37	18·5	i	1·492	0·017	0·038	1·311	3·17	3·74	68
38	18	i	1·538	0·030	0·056	1·272	3·28	3·87	73
39	18·5	ii	1·482	0·108	0·152	0·760	1·66	1·96	62
40	18	i	1·545	0·028	0·053	1·293	3·34	3·94	73
41	18	ii	1·560	0·156	0·200	0·610	1·28	1·51	59
42	20	i	1·486	0·028	0·053	1·234	3·10	3·66	71
43	19	i	1·496	0·035	0·062	1·201	2·93	3·46	70
44	15	i	1·510	0·049	0·081	1·125	2·93	3·40	71
45	17	i	1·492	0·047	0·078	1·121	2·89	3·38	72
46	21·5	i	1·439	0·048	0·079	1·064	2·59	3·08	70
47	20·5	i	1·538	0·041	0·070	1·205	2·90	3·45	69
48	21·5	i	1·439	0·043	0·073	1·092	2·69	3·19	71
			Volume of oxygen admitted = 2·0 c.c. (approx.).						
49	20·5	i	1·990	0·058	0·092	1·553	3·86	4·59	71
50	21	ii	1·986	0·267	0·311	0·508	0·83	0·99	47
51	21·5	i	1·979	0·060	0·106	1·475	3·59	4·27	70
52	22	ii	1·990	0·255	0·299	0·570	0·83	0·99	42
			Volume of oxygen admitted = 2·5 c.c. (approx.).						
53	20	i	2·441	0·090	0·130	1·823	4·55	5·37	71
54	20	ii	2·398	0·348	0·392	0·536	0·83	0·98	44

Note.—The results tabulated here were obtained in two series of experiments, in one of which 5·58 g. of charcoal were used, and in the other 5·575 g. Mass

In Table II are the values for the heat of adsorption of amounts of oxygen varying from 0·5 to 2·5 c.c. (N.T.P.), the temperature of activation throughout this series being 950°, this temperature having been shown by Rhead and Wheeler (J., 1913, **103**, 467) to be necessary for the removal of the oxygen adsorbed at lower temperatures. The results of Table II are summarised in Table III. In the column headed "Adm.," the figures i, ii, and iii indicate whether the admission of gas was a first, second, or third, respectively. In view of a result subsequently to be described, no correction was necessary for the heat developed by the formation of oxides of carbon at the temperature of these experiments.

A separate sample of charcoal was used for each series, and in the second series the charcoal was once replaced by a fresh sample: no difference was observed in the results obtained. The experiments of Table II were not performed in the order shown. The first experiments were made by admitting 1·5 c.c. of gas: after this, 2·0 c.c. and 2·5 c.c. were admitted, followed by several admissions each of 1·0, 0·5, 1·0, and 1·5 c.c.; then admissions of 1·5 c.c. alternated with 1·0 c.c., and, finally, the series closed with an admission of 0·5 c.c.

TABLE III.

Mean Values of the Heat of Adsorption at Room Temperature after Activation at 950°.

Approx. volume of oxygen admitted, c.c. at N.T.P.	Mean heat of adsorption, Cals./mol.		
	(i.)	*(ii.)*	*(iii.)*
0·5	60	55	32
1·0	62	53	40
1·5	70	61	41
2·0	71	45	—
2·5	71	44	—

It will be observed from Table II that repeated adsorption of oxygen at room temperature, followed by repeated activation at 950°, appeared to have no destructive effect on the activity of the charcoal. After the standard activation, the same volume of oxygen was adsorbed and the same amount of heat was evolved even after 30 such admissions and activations. All these results were closely reproducible.

It was shown that no detectable amounts of oxygen were adsorbed on the quartz, glass, platinum, etc. (see p. 2886).

In the earlier experiments of Table II the sample of gas was taken off one minute after admission of oxygen, because this was known to be the time required for the rise of temperature to reach its maximum. It was, however, suspected that adsorption might be [illegible] rapid than the temperature–time curves suggested owing to

the lag involved in the thermometric method. The gas was therefore sampled at a much shorter interval after admission, first at 30, then at 20, at 15, and finally at 10 secs. The order of the residual pressure showed that, with negligible difference, the adsorption had progressed as far in 10 secs. as in 1 min. Other measurements showed that the adsorption of the residual gas was very slow, *e.g.*, whereas 1·125 c.c. were adsorbed in 10 secs., leaving a residue of 0·175 c.c., only 0·066 c.c. of the latter was adsorbed in 48 hours. There was therefore a sudden adsorption of the bulk of gas, followed by a very slow disappearance of the residue. This rapidity of adsorption of a gas on a solid surface is in accordance with theoretical prediction and is characteristic of true adsorption. It has been observed by other workers, *e.g.*, Angus Smith (*Proc. Roy Soc.*, 1862—3, **12**, 424; 1926, *A*, **112**, 296), in the case of oxygen on charcoal; McBain (*Phil. Mag.*, 1909, **18**, 918), for hydrogen on charcoal; and Lamb and Coolidge (*J. Amer. Chem. Soc.*, 1920, **42**, 1146), for various vapours adsorbed on charcoal. In the work of these authors, however, the time periods were of the order of a few minutes. Rhead and Wheeler (J., 1913, **103**, 469), in the case of oxygen on charcoal, observed a rapid disappearance of gas in the first 15 secs., followed by a much slower rate.

Attempts were made to desorb gas from the charcoal immediately after adsorption of oxygen. Such desorption would be indicated by a break in the continuity of the rearward slope, CD (Fig. 4), as shown by the broken line, FGK. For this purpose, the sampling system was employed, the procedure being as follows: A few minutes after maximum temperature had been reached, the tap T_4 was opened, and the reaction vessel rapidly evacuated. No break in the continuity of CD appeared. The adsorbed oxygen was therefore held so tenaciously by the charcoal that at room temperature it could not be removed under a vacuum of 1×10^{-4} mm.

The experiments of this series also showed that the time taken to attain maximum temperature in the case of first admissions varied with the amount of oxygen adsorbed. For admissions of 0·5 c.c. it was 2½ mins., for those of 1·0 c.c. it was 2 mins., and for those of 1·5, 2·0, and 2·5 c.c., 1 min. The corresponding times for second and third admissions were increasingly greater than those for first admissions, but this was doubtless due to the gradual decrease in the energy of the charcoal surface.

Some Experiments with Nitrogen.—Owing to a leak occurring during one of the experiments in the series just described, nitrogen was detected in the gas which was removed from the reaction vessel, and on this occasion a break appeared in CD (Fig. 4), at a point corresponding to the time when the tap T_4 was opened, and

the dotted portion, FGK, of the curve was experimentally realised It was subsequently found possible to reproduce this break at will by admitting mixtures of oxygen and nitrogen. When pure nitrogen was admitted, however, no such break appeared. Thus at room temperature neither pure oxygen nor pure nitrogen could be desorbed, but some gas, which proved to be nitrogen, was desorbed after a mixture of oxygen and nitrogen had been admitted. Some of the data obtained are quoted below, all the adsorptions taking place at room temperature after activation at 950°, and all volumes being reduced to 760 mm. and room temperature.

(1) A first admission of 1·474 c.c. of nitrogen resulted in the adsorption of 0·293 c.c.; from a second admission of 1·545 c.c., 0·248 c.c. was adsorbed. The molar heat of adsorption was estimated at 38 and 19 Cals. respectively. In a third admission, of a mixture of 0·266 c.c. of nitrogen with 1·314 c.c. of oxygen, 1·028 c.c. of gas were adsorbed. A break appeared in CD.

(2) After reactivation, from 1·403 c.c. of nitrogen admitted, 0·223 c.c. was adsorbed with a molar heat of 46 Cals. In a second admission, of a mixture of 0·551 c.c. of nitrogen with 1·225 c.c. of oxygen, 1·152 c.c. of gas were adsorbed. A break was noted in CD.

(3) After reactivation, a mixture of 0·568 c.c. of nitrogen with 1·354 c.c. of oxygen was admitted. Of this, 1·284 c.c. were adsorbed. A break appeared in CD. In a second admission, of 1·567 c.c. of oxygen admitted, 0·436 c.c. was adsorbed. A break appeared in CD, which suggested that some of the oxygen adsorbed in the second admission had replaced the more firmly bound nitrogen, which pumping after the first admission had failed to desorb, and that this nitrogen could now be desorbed by pumping.

(4) After reactivation, 1·538 c.c. of oxygen were admitted, and 1·103 c.c. were adsorbed. Then 1·396 c.c. of nitrogen were admitted, and 0·265 c.c. was adsorbed. No break appeared in CD.

Consideration of the above data leads to the following comments on the respective experiments.

(1) After a total of 0·54 c.c. of nitrogen had been adsorbed, 1·028 c.c. of the mixed gases were still taken up, although the highly active fraction of the surface was already saturated with nitrogen.

(2) Although 0·223 c.c. of nitrogen had already been adsorbed, the charcoal still took up 1·152 c.c. of gas from the mixture of 0·551 c.c. of nitrogen and 1·225 c.c. of oxygen, which is more than would be expected in view of the previous admission of nitrogen.

(3) Similarly in this case, the adsorption of 1·284 c.c. is unexpectedly high.

(4) After adsorbing 1·103 c.c. of oxygen, the charcoal took up

even more nitrogen than in the case of the first admission in (2) above.

It therefore follows that (*a*) nitrogen, like oxygen, is adsorbed at once on a clean charcoal surface, either in first or second admissions, and cannot be removed therefrom at the temperature of adsorption; (*b*) when a mixture of oxygen and nitrogen is admitted, some gas can be pumped from the charcoal surface, irrespective of whether the mixture has been admitted to a clean surface or to one on which nitrogen has already been adsorbed; (*c*) gas can also be desorbed from the charcoal surface in the case of an admission of oxygen following an admission of a mixture of nitrogen and oxygen; (*d*) when nitrogen is adsorbed on a charcoal surface, on which oxygen has already been adsorbed, no gas can be pumped from the surface; and (*e*) the amount of gas adsorbed from a mixture of oxygen and nitrogen appears to be greater than would be expected from what is known of the separate adsorptions of these gases.

This phenomenon has not been thoroughly investigated, but the facts are sufficiently apparent. There is some change in the stability of the adsorption-complexes, formed on the surface of the charcoal, when the oxygen is diluted with nitrogen. This point has already been discussed in Part II.

Other workers have reported somewhat similar effects. De Saussure (*Ann. Physik*, 1814, **47**, 113) noted cases where the presence of a second gas increased the adsorption of a first, and detected the replacement of one gas by another. The latter effect was also observed by Angus Smith (*loc. cit.*).

Heat of Adsorption of very Small Amounts of Oxygen.—The results summarised in Table III indicated a decrease in the heat of adsorption with decrease in the amount of gas admitted. To test the possibility of this heat being still less for lower concentrations of gas, very small amounts of oxygen were admitted, and attempts made to determine their heats of adsorption. The experiments showed that at these low concentrations the oxygen was adsorbed completely without, as far as this apparatus indicated, any appreciable rise of temperature. A typical result may be quoted, all volumes being at normal pressure and room temperature. After activation at 950°, 0·036 c.c. was admitted at room temperature. When the gaseous contents of the reaction vessel were sampled according to the usual method, no increase in the pressure was recorded. The McLeod gauge still registered high vacuum. A second admission of an equal amount of gas gave the same result. A third admission of 0·089 c.c. and a fourth of 0·071 c.c. gave appreciable rises of temperature, with residues of unadsorbed gas of 0·001 and 0·003 c.c. respectively. Two further experiments

confirmed this result. The first minute quantities of oxygen wei therefore adsorbed with a very low heat of adsorption, which wa apparently less than 5 Cals./mol.

Immediately following these experiments with small quantitie and after re-evacuation, 1·5 c.c. of oxygen were admitted. In a cases the normal value was obtained for the heat of adsorptioı and no reduction in the adsorptive capacity of the charcoal wa apparent beyond that due to the amount of gas already adsorbec

A test was made to determine whether the small amounts c oxygen had been removed by the platinum, quartz, etc. Th charcoal was taken out of the apparatus and the process of activatio carried out in its absence; 0·036 c.c. of oxygen was then admittec and the volume of the apparatus was calculated from the resultin pressure as recorded by the McLeod gauges, but did not differ b more than the experimental error from the known volume, and thu showed that these small amounts of oxygen were adsorbed on th charcoal and not on any of the parts of the apparatus.

Heat of Adsorption of Oxygen on Charcoal from Room Temperatur to 200°.—In Table IV are the values obtained for the heat of adsorp tion of oxygen on charcoal at various temperatures from rooı temperature to 200° after activation at 950° in each case. The sam sample of charcoal was used throughout the experiments of thi series: it was not so active as that used previously, *e.g.*, at 20° of 3·0 c.c. (N.T.P.) of oxygen admitted, only 1·4 c.c. were adsorbed The heat of adsorption had, however, the same value as that pre viously found for that temperature.

The increment of temperature recorded in the table is the net increment of temperature due to adsorption, *i.e.*, the difference between the (corrected) rise of temperature observed and that due to the "gas effect." The correction for the latter varied from 0·25° to 0·30°, *i.e.*, it was of the order of 10% approximately. The values given for the heat evolved are corrected for the heat of formation of the amounts of oxides of carbon found by analysis, except in the experiments at 60° and 100°, in which analyses were not made. This correction in the experiments at 150° and 200° amounted to 5% of the heat evolved. In Experiments 60 and 62 the residual pressure was not read until some minutes after adsorp tion had occurred, and in both these cases the tap T_5 was left open, not for 10 seconds as in the usual case, but for several minutes until a constant pressure was recorded by the McLeod gauges.

In these experiments it was found that at the higher temperatures the adsorption required about 1 min. for completion and therefore was not so rapid as at room temperature, where the adsorption

Table IV.

Heat of Adsorption of Oxygen on Charcoal from Room Temperature to 200°.

Expt	Temp. of charcoal.	Temp. of room.	Oxygen *admitted*, c.c.	Pressure of sample (mm.), obs.	Pressure of sample (mm.), corr.	Oxygen *adsorbed*, c.c.	Rise *of* temp.	Heat *evolved*, g.-cals.	Heat of *adsorption*, Cals./mol.
55	20°	20°	3·035	0·298	0·342	1·397	3·48°	4·04	70
56	57	19	1·073	0·009	0·023	0·964	2·81	3·71	92
57	57	21·5	1·066	0·011	0·027	0·938	2·63	3·47	89
								Mean =	91
58	96	14	1·066	0·0008	0·0023	1·055	3·33	5·00	112
59	97	16·5	1·059	0·001	0·003	1·045	3·28	4·92	112
60	97·5	19·5	1·130	—	0·020	1·036	2·89	4·34	101
61	97·5	18·5	1·123	0·003	0·009	1·081	3·22	4·83	107
62	97·5	18·5	0·995	—	0·012	0·939	2·83	4·25	108
								Mean =	108
63	150	18	1·038	0·004	0·012	0·982	2·92	4·68	114
64	200	21	1·073	0·010	0·024	0·962	2·67	4·57	115
65	200	20	1·059	0·0078	0·020	0·967	2·67	4·65	116
66	200	20·5	1·066	0·0078	0·020	0·974	2·71	4·72	117
								Mean =	116

Note.—Mass of charcoal = 5·45 g. Mass of platinum = 6·665 g. All volumes are referred to normal pressure and room temperature.

here studied was complete in less than 10 secs. This may possibly be due to the blanketing effect of the oxides of carbon evolved.

Gaseous Products of the Adsorption of Oxygen on Charcoal.—The results of the analyses carried out in the experiments at 18°, 150°, and 200° were as follows:

Temp. of adsorption.	Gaseous products.
18°	Oxygen; trace of CO_2; no CO.
150	5% Oxygen; 95% CO_2; trace of CO (?).
200	9% Oxygen; 82% CO_2; 9% CO.

There was thus residual oxygen over the whole range of temperature of these experiments. Carbon dioxide increased up to 150°, and then decreased while the monoxide increased.

The "Active" Fraction of the Surface of Charcoal.—The "active" fraction of the surface of the charcoal used in these experiments may be estimated from the results of Table II. Its total surface was determined, from the isotherms of straight-chain alcohols adsorbed thereon (Garner, McKie, and Knight, *J. Physical Chem.*, 1927, **31**, 641), as 66 sq. m. per g. The volume occupied by an atom of carbon in charcoal is $1/D \div N/12$, where D is the density, and N the Avogadro number, $6{\cdot}062 \times 10^{23}$. On insertion of the value for D obtained by Cude and Hulett (*J. Amer. Chem. Soc.*, 1920, **42**, 391), *viz.*, 1·9, it is found that this volume is 1×10^{-23} cm.^{3}. If, as a first approximation, this space be assumed cubical, the

cross-sectional area corresponding to every atom of carbon $4{\cdot}64 \times 10^{-16}$ cm.^{2}. The number of atoms on the surface of 1 of charcoal is, therefore, $66 \times 10^4/4{\cdot}64 \times 10^{-16} = 1{\cdot}4 \times 10^{21}$. T total number of atoms in 1 g. of charcoal $= N/12 = 5{\cdot}05 \times 1($ Therefore, the ratio of surface atoms to total atoms $= 1{\cdot}4 \times 10$ $5{\cdot}05 \times 10^{22}$, or 1 to 36.

Table II shows tbat at the most 2 c.c. (N.T.P.) of oxygen can adsorbed by 5·6 g. of charcoal with a molar heat of adsorption the order of 70 Cals. On the assumption that every molecule oxygen is adsorbed on one atom of carbon only, and since t number of molecules in 1 c.c. (N.T.P.) of oxygen is $2{\cdot}7 \times 10^{19}$, t number of atoms per gram of charcoal giving a molar heat adsorption of 70 Cals. $= 2 \times 2{\cdot}7 \times 10^{19}/5{\cdot}6 = 1{\cdot}0 \times 10^{19}$ (nearl If these are regarded as active atoms, the ratio of active to to atoms is $1{\cdot}0 \times 10^{19}/5{\cdot}05 \times 10^{22}$, or 1 in 5000, and the ratio active atoms to surface atoms is $1{\cdot}0 \times 10^{19}/1{\cdot}4 \times 10^{21}$, or 1 in 1

This value for the active fraction of the surface is in qualitati agreement with the general results obtained by Langmuir, w found that these fractions were generally small, and that th increased with the temperature at which the surface was clean Table I confirms this latter effect for the charcoal employed in tl work, for it is there shown that the proportion of oxygen adsorb at room temperature from a constant volume admitted increas steadily with the temperature of activation. The amount of g adsorbed will depend, however, on two factors : (1) the temperatu of activation, and (2) the efficiency of the process for removal adsorbed gases.

The activity of the charcoal used in these experiments may compared with that of the charcoal used by Keyes and Marsh (*J. Amer. Chem. Soc.*, 1927, **49**, 156). From the curve obtained l plotting the heat of adsorption against the surface concentration oxygen, these authors calculated that the active surface of th charcoal was 5100 cm.^{2} per g. This value is in good agreeme with that obtained in this work, *viz.*, 4700 cm.^{2} per g. Keyes a Marshall, however, concluded that, at the highest concentration which they worked ($4{\cdot}5 \times 10^{-4}$ mol. per g.), many layers of g were present. Their highest concentration is equivalent to 4·5 22400×10^{-4} c.c. of oxygen per g. of charcoal, *i.e.*, 10 c.c. per From the value here recorded for the total surface area of 1 g. charcoal, the number of molecules of oxygen necessary to form unimolecular layer thereon is $66 \times 10^4/\pi \times (1{\cdot}81 \times 10^{-8})^2$, sin the radius of the oxygen molecule is 1·81 Å. (Jeans, "Dynamic Theory of Gases"); but the number of molecules in 1 c.c. (N.T.P is $2{\cdot}7 \times 10^{19}$, hence the volume of oxygen required to form a un

molecular layer = 24 c.c. per g. of charcoal, or more than twice the highest concentration measured by Keyes and Marshall. There is thus no evidence in their work of the formation of a second adsorbed layer, or even of the completion of a first layer. Moreover, their experiments did not indicate that their charcoal was saturated.

Summary.

A method is described for measuring the heats of adsorption of gases on solid surfaces, and is applied to the study of the adsorption of oxygen and of nitrogen on charcoal.

Details of a specially devised apparatus and furnace are given.

In conclusion, the author wishes to express his thanks to the Advisory Council of the Department of Scientific and Industrial Research for a maintenance grant, which enabled him to carry out the earlier part of this work, and to Prof. W. E. Garner for his constant help and direction during its progress.

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CCCLXXXI.—*The Ionisation of Aromatic Nitro-compounds in Liquid Ammonia. Part II.*

By WILLIAM EDWARD GARNER and HENRY FRANK GILLBE.

THE aromatic dinitro-compounds undergo ionisation in liquid ammonia at measurable speeds (Part I, Field, Garner, and Smith, J., 1925, **127**, 1227), giving rise to solutions the molecular conductivities of which are comparable in magnitude with those of typical electrolytes in this solvent. At moderately high dilutions, the ionisation is nearly complete. The rates of ionisation of the *m*-derivatives, as determined by conductivity measurements, are in agreement with the equation for reactions of the first order, whereas those of the *o*- and *p*-derivatives change in accordance with the equation for reactions of zero order. The *m*-compounds become faintly coloured immediately after solution, and blue or purple when the ionisation has reached its equilibrium value: the *o*- and *p*-derivatives are colourless initially and yellow or brown at the end of the ionisation. These colour changes are of interest in that they accompany changes in conductivity and hence may be due to the production of ions. If the ions only are coloured, then it should be possible by measurements of the extinction coefficients of the

solutions to determine their concentration and to examine t relationship between ionic concentration and conductivity.

The absorption spectra of the *m*-dinitro-compounds show t bands, one in the yellow and one in the near ultra-violet, bo increasing in width as the ionisation proceeds. In the case of t first band, this increase is due mainly to a movement of the le refracted edge. This is seen in photographs (Fig. 1) of the absorpti spectra of solutions of *m*-dinitrobenzene taken at various times aft the preparation of the solution. The neon spectrum photograph on the same plate provides a means of measuring the change in t width of the adsorption bands with time. A simple relationsh holds between the wave-length of the edge of this band and t conductivity, *viz.*, $(\lambda_0 - \lambda_t)/\mu_t =$ constant, where λ_0 and λ_t are t wave-lengths (in Å.U.) of the edge of the band at the commenceme of ionisation and at time t (in mins.), respectively, and μ_t is t product of specific conductivity (in mhos) and dilution at time t (s Table I). The dilution was in all cases 416·2 litres, and the valu

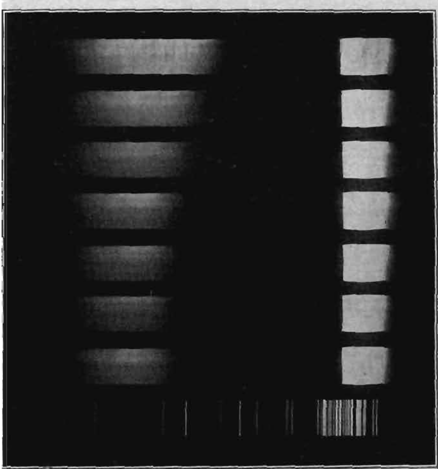
TABLE I.

m-Dinitrobenzene. $\lambda_0 = 4891$.				2 : 4-Dinitrotoluene. $\lambda_0 = 5490$.			
t.	μ_t.	λ_t.	$(\lambda_0 - \lambda_t)/\mu_t$.	t.	μ_t.	λ_t.	$(\lambda_0 - \lambda_t)/$
10	96·8	4592	3·09	66	71·9	5116	5·20
13	109	4559	3·04	71	75·6	5100	5·15
17	118	4527	3·08	95	89·0	5035	5·12
20	123	4512	3·08	134	104·6	4948	5·17
24	126	4500	3·10	190	118·0	4868	5·27
29	130	4497	3·03	254	126·0	4826	5·26
36	131	4496	3·01	303	130·0	4806	5·25
3 : 4-Dinitrotoluene. $\lambda_0 = 4160$.				3 : 5-Dinitrotoluene. $\lambda_0 = 5000$.			
72	1·55	4515	229	16	52·8	4731	5·10
84	1·72	4552	228	20	55·7	4716	5·10
116	2·18	4674	235	25	58·8	4702	5·07
160	2·81	4815	233	32	61·5	4689	5·05
217	3·63	4995	230	42	62·8	4680	5·10

of the specific conductivity are taken from the previous pap (*loc. cit.*).

The above relationship between the change in the wave-length o the edge of the absorption band and the conductivity is readil understood if both of these properties are directly proportional t the concentration of the ions. The movement of the edge of th charged with change in concentration is not necessarily linear i unimolecular; the nature of the relationship depends on the type o the radius phic plate used and its sensitivity to light of differen Theory of Gaphs. The constancy of $(\lambda_0 - \lambda_t)/\mu_t$ is therefore ver is $2{\cdot}7 \times 10^{19}$, fitous. It does suggest, however, that both $\lambda_0 - \lambda_t$ an

Fig. 1.



[To face p. 3890.]

μ_t are very possibly directly proportional to the concentration of a coloured ion. In order to settle this point definitely, it is necessary to make measurements of the extinction coefficients of monochromatic radiation passing through the solution. These have now been made at constant temperature (at or near $-35°$) for a number of wave-lengths with *m*-dinitrobenzene, and at one wave-length for 2 : 4-dinitrotoluene.

The extinction coefficient E may be defined by the equation $I/I_0 = e^{-Ecd}$, and if Beer's law be assumed to hold for these solutions, from one value of c and measurements of I/I_0 over a period of time, the change in concentration of the coloured substance can be followed. Such measurements are now described (see Experimental).

For this series of experiments, the concentrations of nitro-compounds were chosen in the region where ionisation is practically complete (94—96%), and hence the final ionic concentration will be the same as the initial concentration of the nitro-compound. The concentrations (c, in mols./l.) of the coloured substance calculated from this value and from measurements of I/I_0 are given in Table II. The ratio of conductivity l_t to c_t is constant. The conductivities of the solutions were measured between two platinum electrodes, and, in the case of 2 : 4-dinitrotoluene, simultaneously with the measurements of extinction coefficients. The cell constant was not

TABLE II.

m-Dinitrobenzene.

$v = 5880$; temp. $= -34{\cdot}5°$.

t.	$10^7 . c_t$.*	v.	l_t.	$l_t/c_t . 10^{-4}$.
3	974	10,270	875	899
6	1301	7,690	1128	867
9	1445	6,920	1310	907
15	1587	6,300	1498	944
20	1638	6,110	1545	944
25	1660	6,020	1560	939
30	1682	5,950	1570	934

* Mean of values at 4340 and 4192 Å.

2 : 4-Dinitrotoluene.

$v = 4170$; temp. $= -34°$; $\lambda = 4650$ Å.

t.	$10^7 . c_t$.	l_t.	$l_t/c_t . 10^{-5}$.
20	520	1082	208
40	876	1756	200
60	1236	2590	209
90	1436	3072	214
120	1820	3612	198
150	2040	4012	197
190	2140	4430	207
230	2268	4784	211
270	2240	4896	219
300	2330	5050	217

$v = 4340$; temp. $= -35{\cdot}1°$; $\lambda = 4650$ Å.

t.	$10^7 . c_t$.	l_t.	$l_t/c_t . 10^{-5}$.
20	407	985	242
40	773	1810	234
90	1342	3284	245
120	1534	3842	250
150	1748	4270	244
190	1919	4656	243
230	2064	5050	245
270	2110	5242	248

measured, hence the values for the conductivity are given i arbitrary units.

The concentration of the coloured substance as determined fro the extinction coefficients is directly proportional to the conductivit of the solution at all stages during the process of ionisation. Tl colour of the solutions of *m*-dinitro-compounds is therefore due t the ions and not to any other substances formed during the ioni ation; *thus, the rate of production of the coloured ions in the compounds* obeys the equation for reactions of the first order.

The ions present in these solutions were shown previously to l the nitro-compound in the form of an anion, and positively charg ammonia molecules as kations. Since the colour varies from o nitro-compound to another, the coloured ion must be the anion.

Nature of the Ionisation in Solutions of Nitro-compounds in Liquid Ammonia.

The majority of substances dissolved by liquid ammonia obey tl law of mass action in their ionisation much better than those aqueous solutions. The law of mass action holds fairly accurate for dilute solutions of liquid ammonia (Kraus, "Properties Electrically Conducting Systems," p. 56). On applying the equatio $K_1 = \alpha^2/v(1-\alpha)$ and $K_2 = \alpha^3/v^2(1-\alpha)$ to Franklin's values of t molecular conductivity of *m*-dinitrobenzene in liquid ammonia, it found that K_1 gives a much better constant than K_2 (Table III).

TABLE III.

v.	μ.	K_1.	$K_2 \times 10^4$.	v.	μ.	K_1.	$K_2 \times 1$
12·38	45·7	0·0044	0·74	188·4	100·0	0·0024	0·06
24·42	53·35	0·0032	0·32	380·0	131·7	0·0024	0·04
43·30	71·5	0·0036	0·27	752·0	156·4	0·0023	0·02
95·40	90·2	0·0030	0·13	1485·0	179·9	0·0024	0·01

The dissociation constant K_1 is very similar to that of typi binary salts in ammonia; *e.g.*, for ammonium chloride, $K = 0·001$ for potassium bromide, $K = 0·0022$; and for potassium nitra $K = 0·0017$ (Franklin and Kraus, *Amer. Chem. J.*, 1900, **23**, 29 The evidence is thus in favour of the view that the ionisation dinitro-compounds in liquid ammonia is of a binary character.

It was shown previously that one of the ions was in all probabil NH_3^{++} (or $N_2H_6^{++}$), since no trace of any substance was detecta at the cathode either during or after electrolysis of a solution *m*-dinitrobenzene in ammonia. Hence *it was suggested that* ionisation process was

$$R(NO_2)_2 + NH_3 \overset{(I)}{\rightleftharpoons} R(NO_2)_2,NH_3 \overset{(II)}{\rightleftharpoons} R(NO_2)_2^{--} + NH_3^{++} \quad (1$$

On the basis of the Lewis–Langmuir octet theory, it is more probable that the ammonia ion is $N_2H_6^{++}$, and that the equation should be

$$R(NO_2)_2 + 2NH_3 \overset{(I)}{\rightleftharpoons} R(NO_2)_2,2NH_3 \overset{(II)}{\rightleftharpoons} R(NO_2)_2^{--} + N_2H_6^{++} \quad (2)$$

Attempts were made to prepare the intermediate compound, $R(NO_2)_2,2NH_3$, which might be stable in the solid state. A vapour-pressure method was used at temperatures in the neighbourhood of −40°, but no evidence was obtained for the existence of such a compound. It is, however, necessary to assume the formation of an intermediate compound during the ionisation process, otherwise it is impossible to explain the fact that the rate of ionisation of 2 : 6-dinitrotoluene, which is only ionised to the extent of about 2% at 400 litres, obeys the first-order law. Equation (3) is therefore unlikely :

$$R(NO_2)_2 + 2NH_3 \rightleftharpoons R(NO_2)_2^{--} + N_2H_6^{++} \quad . \quad (3)$$

If this equation represented the course of the reaction, the occurrence of the preponderating reverse reaction would prevent a constant being obtained for the equation $k = 1/t \, . \log_e a/(a - x)$.

This applies to a less degree also to the other dinitro-compounds, which are not completely ionised at dilutions of 400 litres (compare Part I, *loc. cit.*). Thus, we are driven to the conclusion that the stage in the reaction which determines the order is not the ionisation process, and therefore we postulate the formation of an intermediate compound [stage (I), reaction (2)].* Whatever the nature of this reaction, since it obeys the first-order law, it must go to completion.

In the previous paper, the equation

$$k = 1/t \, . \log_e \mu_e/(\mu_e - \mu_t) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where μ_e and μ_t are the molecular conductivities of the solutions at the end of the reaction and at a time t, respectively, was applied to the changes in conductivity in solutions of nitro-compounds. This equation is only strictly accurate, when applied to reaction (2), if the dilutions are such that the ionisation is complete. When the ionisation is incomplete, the conductivity is no longer an exact measure of the amount of intermediate compound produced, and equation (4) requires modification. If α_e and α_t represent the degrees of ionisation at equilibrium and at a time t, respectively, then the equation

$$k = \frac{1}{t} \log_e \frac{\mu_e/\alpha_e}{\mu_e/\alpha_e - \mu_t/\alpha_t} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

* The critical increment of the reaction, which is found to be 7,520 calories, is that corresponding to chemical change rather than to an ionisation process, for which a much larger value is probable.

would be expected to be more nearly correct than equation (4). The values of α may be obtained from the specific conductivities of Franklin by plotting κ against α. Table IV shows the effect of applying equation (5) to the velocity measurements for *m*-dinitrobenzene.

TABLE IV.

t.	μ.	κ.	α.	μ/α.	k.	k (Part I).
10	84·3	0·404	0·556	152	0·107	0·140
12	89·4	0·429	0·542	165	0·105	0·133
16	98·3	0·471	0·520	189	0·109	0·131
22	106·0	0·508	0·500	212	0·114	0·133
10	96·8	0·232	0·687	141	0·109	0·132
13	109	0·262	0·660	165	0·116	0·134
17	118	0·283	0·645	183	0·115	0·132
22	123	0·296	0·635	194	0·112	0·134
24	126	0·302	0·630	200	0·117	0·129

For those nitro-compounds which are ionised considerably in liquid ammonia, the use of equation (5) does not improve the constancy of k. There is, however, an appreciable source of error in interpolating from Franklin's results. In the case of 2 : 6-dinitrobenzene, where the ionisation is much less complete, there is a marked improvement in constancy. To make this calculation, it is assumed that the conductivity at infinite dilution is the same for 2 : 6-dinitrotoluene as for *m*-dinitrobenzene. Such an assumption is justifiable since the introduction of a methyl group into a heavy aromatic molecule would have but little effect on the mobility of the anion. The following results are thus obtained :

t	11	54	108	162
k	0·015	0·015	0·014	0·015
k (Part I)	0·028	0·021	0·017	0·015

The very feebly ionised 2 : 6-dinitrotoluene gives a good constant when k is calculated from equation (5). The assumptions made above with respect to the mechanism of the ionisation process have been justified by all of the facts at our disposal.

The values of k calculated from the measurements at higher dilutions, $v = 4000$, where α does not change appreciably during the reaction, agree within experimental error (see results for 2 : 4-dinitrotoluene, Table VII).

Thus equation (2) represents in a satisfactory manner the course of the reaction. The first stage is a slow reaction which goes to completion, and the second stage is rapid and proceeds to equilibrium. At moderate concentrations, the ionisation is not complete. The characteristic colour of these solutions is due to the anion, which is very probably $R(NO_2)_2^{--}$. There is a direct proportionality between the conductivity of the solutions and the concentration of the anion at any time during the course of the reaction.

EXPERIMENTAL.

Preliminary Absorption Measurements.—A simple form of apparatus was used consisting of a light-tight wooden box with a tightly fitting lid; at one end was fixed a 250-c.p. Pointolite lamp, and at the other an unsilvered Dewar vessel of about 280 c.c. capacity, which could be wedged tightly against a hole of about 2 cm. diameter at the end of the box. The light passing through the Dewar vessel fell on the slit of a Hilger constant-deviation spectrometer.

The Dewar vessel was nearly filled with liquid ammonia, and a known amount of nitro-compound added, either as a solid or in solution in 1 or 2 c.c. of ethyl alcohol. Photographs were taken after varying intervals of time on the same plate (Fig. 1). The addition of the nitro-compounds in solution ensured a greater rapidity of admixture, and the presence of a small quantity of alcohol did not affect the rate of ionisation. With the slit at 0·15 mm., and with Ilford Panchromatic plates, an exposure of ½—1 minute was found to be ample for the dilutions used. For ease in determining the edges of the absorption bands, a neon spectrum was photographed above and usually below each series of spectra.

Although the plates were panchromatic, the intensity of the image obtained with the light passing through liquid ammonia alone was not quite uniform from one end of the spectrum to the other, especially in the green. The image was, however, sufficiently uniform for the purpose of the above measurements, since the movement of the edge of the bands occurred over a narrow region of the spectrum.

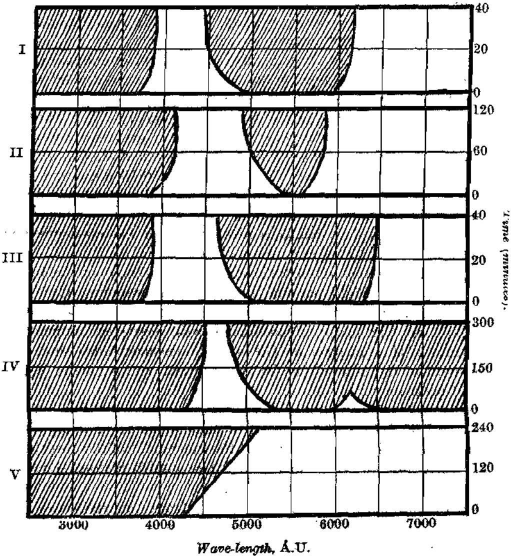
Experiments were made with *m*-dinitrobenzene and 2 : 4-, 2 : 6-, 3 : 5-, and 3 : 4-dinitrotoluenes at a dilution of 416·2 litres. The position of the absorption bands and the movement of the absorption edges with time are given in Fig. 2. The shaded regions show the absorption bands.

One or two points of interest emerge from the spectrum–time diagrams (Fig. 2). All the *m*-dinitrotoluenes and *m*-dinitrobenzene show absorption bands at about 3000—4000 Å. In all cases the bands widen with time. The introduction of a methyl group in the meta-position to two nitro-groups (I and III) has hardly any effect either on the position or on the velocity of movement of the edge of the bands. If this group is ortho to one of the nitro-groups (IV), the band in the yellow narrows; and if it is ortho to two nitro-groups (II), the band is narrower still. Nitro-groups ortho or meta to a methyl group have but little effect on the position of the ultra-violet band, whereas the introduction of a *p*-nitro-group (IV) shifts this edge towards the red and also causes the appearance of an

absorption band in the extreme red. The absorption edge of 3 : 4-dinitrotoluene moves linearly with time.

Molecular Compounds.—It was considered possible that compounds of the type $R(NO_2)_2,xNH_3$ might be stable in the solid state, especially as the solids separating on evaporation of the ammonia solutions

Fig. 2.



I. m-*Dinitrobenzene.* II. 2 : 6-*Dinitrotoluene.* III. 3 : 5-*Dinitrotoluene.* IV. 2 : 4-*Dinitrotoluene.* V. 3 : 4-*Dinitrotoluene.*

appeared to be coloured. Vapour-pressure measurements made on solutions of both the *m*- and the *o*- and *p*-derivatives during the process of evaporation failed to yield any evidence of the occurrence of such compounds in the solid state. A range of temperature down to $-48°$ was covered.

Critical Increment of Reaction.—From conductivity measurement of solutions of *m*-dinitrobenzene in liquid ammonia over a range o

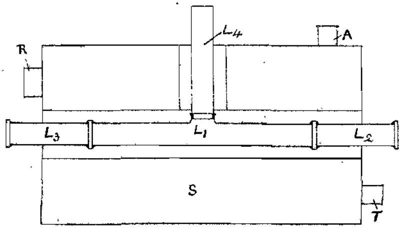
temperatures, the critical increment of the reaction was shown to be 7,520 cal. The corresponding velocity coefficients were :

Temp.	− 34·4°	− 39·3°	− 41·3°	− 44·5°
k	0·176	0·133	0·116	0·087

The wave-length corresponding to the energy of activation lies in the infra-red at 3·78 μ. The change was not accelerated by the light from a mercury-vapour lamp.

Measurement of Extinction Coefficients.—To make measurements of extinction coefficients, it was necessary to enclose a known volume of solution in a vessel maintained at constant temperature and having optically worked windows at a known distance apart. The final form of the apparatus is shown in Fig. 3. The constant-temperature bath consisted of a welded, mild-steel tank, S, measuring about 6″ × 4″ × 4″, filled with commercial ammonia; R is an

FIG. 3.



opening for a temperature regulator and air vent, T an opening for an alcohol thermometer, and A the air inlet. The temperature was controlled by regulating a stream of air, bubbling through the ammonia, by means of a relay and magnetic cut-off. The thermostat was heavily lagged with felt.

The reaction vessel consisted of four parts, L_4 fitting into L_1 by means of a ground joint, and the end portions L_2 and L_3 being attached to L_1 by means of guttapercha and separated by polarimeter plates. L_2 and L_3 projected some distance beyond the ends of the tank and their end plates prevented condensation of water vapour on the ends of L_1 during the measurements. Guttapercha was found to be the only suitable cement at −35° for attaching the polarimeter plates; other adhesives either cracked at the low temperature or were attacked by liquid ammonia.

The tank was placed in position between a Hilger constant-deviation spectrograph and a light-tight wooden box containing

a Pointolite lamp and a condensing lens system. The curre through the lamp was maintained constant to 1 part in 500 par The width of slit found to be most satisfactory was 0·15 mm.

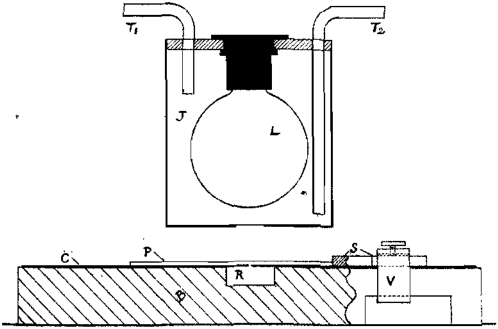
The experimental procedure was as follows : (1) The tank w filled with commercial ammonia and the temperature adjusted the required value. (2) The reaction tube was filled with pu ammonia. (3) A trial exposure was made in order to ensure th there was even illumination along the length of the collimator sli it was impossible to determine this visually. (4) A series of phot graphs was taken with exposures varying from 5 seconds to 1 minu of that part of the spectrum at which it was intended to ma measurements, with a neon spectrum above and below the seri During this operation the rest of the plate was screened with a th piece of cardboard. (5) The dark slide was moved a certain distan horizontally, and the card screen removed. (6) A known volume an alcoholic solution of the dinitro-compound under investigati was added to the reaction tube and the volume made up immediate to a mark on the vertical tube, L_4. At this moment a stop-watch w started, and the first exposure made as soon as possible. A series photographs was then taken over the whole period of the reaction- about 30 minutes in the case of *m*-dinitrobenzene—an exposure 1 minute being given in each case. As only 6 or 7 photograp could be taken on one plate, the earlier ones were taken at short intervals than those at the end of the reaction, since at the beginni the spectrum was changing most rapidly. Photographs were ther fore taken at about 2, 5, 9, 14, 19, 24, and 30 minutes from th commencement of the reaction. (7) Photographs of the ne spectrum were taken immediately above and below the reacti exposures.

It was intended to make simultaneous measurements of th conductivities of the solutions, but owing to the short time taken f the reaction to go to completion, this was not always possible. Th final experiments were made with 2 : 4-dinitrotoluene, which tak some 5—6 hours to attain equilibrium. In this instance, co ductivity measurements could without difficulty be made simu taneously with the photographs of the absorption spectra. In oth cases, conductivity measurements were made separately.

Measurement of the Plates.—The densities of the photograph images were measured by means of a thermopile connected to a Mo galvanometer with the usual lamp and scale. The apparatu constructed for this purpose is shown in Fig. 4. The thermopi (not shown) was fixed rigidly in the recess, *R*, in the wooden bloc *B*, the leads being taken out through the sides of the block. Attache to the surface of the block was a sheet of blackened card, *C*, having

lit immediately above the thermopile element about 1 mm. wide and omewhat shorter than the width of one of the spectral images on the hotographic plate. At a short distance above the slit was clamped "Fullolite" lamp, L, surrounded by a blackened glass tank, J, aving a clear circle at the bottom. A rapid stream of water at onstant temperature could be circulated through the tank *via* the ubes T_1 and T_2. This ensured the removal of infra-red radiation rom the beam which reached the thermopile; errors would other-vise have been introduced by the gradual heating of the apparatus, nd by variations in the thickness of the glass plate, since glass shows narked absorption in the infra-red.

FIG. 4.



It was necessary to ensure that the same wave-length band would e measured for each of the spectra of a series, *i.e.*, that the movement f the plate necessary to bring successive spectra of a series over he slit was in a direction at right angles to the length of the spectra. This was accomplished by preparing a number of steel strips with ccurately parallel edges and of known width, from about $\frac{1}{8}''$ to $\frac{1}{2}''$ wide. A steel straight edge was clamped to the block B in such a osition that when the plate to be measured was moved with one dge always in contact with the straight edge, corresponding lines n the two neon spectra could be superimposed in succession on the lit above the thermopile element. Measurements of the spectral mages at the wave-length of this line could thus be carried out. By lacing between the straight edge and the edge of the plate one or nore of the steel strips, further series of measurements at other

wave-lengths could be made. In the figure, two of the steel strip are shown held in position by the clamp, V. P represents a plate i position for measurement.

Knowing the rate of change of wave-length along the neo spectrum, together with the width of the steel strips used, the wave lengths at which the measurements had been made could be cal culated. Measurements were made at the same wave-lengths fo the calibration exposures as for the exposures made during th reaction. In all cases the galvanometer deflexions were taken as th plate was moved backwards and forwards above the slit.

Having measured the densities of the images given by the cali bration exposures and by the "reaction exposures" (at the sam wave-lengths), one can calculate the fraction of light transmitte through the solution at any time. In the calculation which follows it is assumed that the density of the image is directly proportiona to the total quantity of light energy falling on the plate, an assump tion which, although not rigidly true, is approximately so over . certain range of exposures [compare Baly, *Proc. Roy. Soc.*, 1927, *A* **113**, 711, for a critical investigation of the Schwarzschild equatior $D = kIT^n$; the statement is there made that the results "woul seem definitely to establish that the Schwarzschild exponen (n) is unity"]. In all the measurements with *m*-dinitrobenzene, th calibration curves obtained by plotting time of exposure agains galvanometer deflexion are straight lines over the range employe in the further calculation.

In Table V are given the calibration figures for Plates I and II, fo *m*-dinitrobenzene; T is the time of exposure in seconds, and unde the various wave-lengths are given the galvanometer deflexions fo each image. A is the intercept of the calibration line on the de flexion axis, and $b/60$ the slope of the line (in secs./cm.) divided b 60, a quantity which is required in the subsequent calculation of th extinction coefficients.

TABLE V.

	Plate I.				Plate II.		
T.	Deflexions at λ (Å.U.).				Deflexions at λ (Å.U.).		
	4340.	4192.	4560.	4140.	4340.	4192.	4560.
5	169	177	50	209	276	201	144
10	151	157	37	187	254	181	127
15	130	136	26	168	—	—	—
20	114	122	15	146	217	144	96
25	92	100	6	125	194	126	80
30	76	84	4	111	180	114	61
35	60	74	3	106	166	109	47
40	—	—	—	—	162	106	32
A =	*188*	*196*	*62*	*230*	*296*	*220*	*162*
$b/60 \times 10^4$ =	4387	4387	6945	3970	4107	4366	5061

Let D = density of image, I = intensity of light falling on the ıotographic plate, and d = galvanometer deflexion due to the ıage. Then, for the calibration exposures

$$D_n = kT_nI_0 = k'(A - d_n) \quad . \quad . \quad . \quad . \quad (6)$$

ıce on plotting T against d for the calibration exposures a straight ıe is obtained; n refers to the number of seconds. In this case is constant and T variable.

For the "reaction exposures" $D_t = kT_0I_t$, where T_0 is constant = 60 secs.), and I_t, the intensity of light transmitted by the solution time t, varies as the reaction proceeds. Further, we may write

$$D_t = k'(A - d_t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

ıere A is the deflexion for the plate when exposed to light of zero tensity, and is necessarily the same as in equation (6).

The quantity required is I_t/I_0, the fraction of the incident light ansmitted through the solution at time t. From equations (6) ıd (7)

$$\frac{I_t}{I_0} = \frac{(A - d_t)T_n}{(A - d_n)T_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

ıt $T_n/(A - d_n)$ is the slope of the line obtained by plotting T ;ainst d for the calibration exposures, in sec./cm. Putting this ıual to b, and substituting for T_0 = 60 secs., we have

$$I_t/I_0 = b(A - d_t)/60 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The extinction coefficient is defined by E in the equation

$$I = I_0e^{-Ecd'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

ıere I/I_0 is the fraction of light transmitted through a layer of lution of thickness d' and concentration c.

If it be assumed that the reaction between the dinitro-compound ıd ammonia goes to completion, the concentration at equilibrium ll be the concentration of the nitro-compound added initially, and e value of E can be calculated by taking the extrapolated value I/I_0 at equilibrium, and substituting the necessary values in uation (10). The figures obtained for E are given in Table VI.

The extinction coefficient E being known, the change in concenıtion of the absorbing substance can be determined by transrming equation (10) thus

$$c = -(1/Ed') \,.\, \log I/I_0 \quad . \quad . \quad . \quad . \quad . \quad (11)$$

ıd this gives the values of c appearing in Table VI (cols. 3 and 6). By substituting the calculated values of c in the unimolecular rmula

$$k = 1/t \,.\, \log_e (c_0 - c_e)/(c_t - c_e) \quad . \quad . \quad . \quad (12)$$

where c_0 is the initial, and c_e the equilibrium concentration, and c_t th concentration at time t, we obtain a similar velocity coefficient t that resulting from the conductivity measurements (see Table V cols. 4 and 7). The high initial values of k are probably due t difficulties in mixing, but any error in the zero time would affe measurements of extinction coefficients and of conductivity equall

By interpolating values of the specific conductivity at the sam temperature and times as the calculated concentrations, the mole ular conductivities can be calculated. These are summarised i Table II: v is the dilution, l_t the interpolated specific conductivit and in the last column is given a value proportional to molecula conductivity, which is practically constant over the range of dilutior concerned. Franklin (*Z. physikal. Chem.*, 1909, **69**, 272) finds change of only about 2% over this range of dilutions, which is le than the experimental error.

Results.

The thickness of the solution was in all cases 3·83 cm., being th length of the middle portion L_1 of the reaction tube (Fig. 3). Th concentrations given in Tables VI and VII are in g.-mols. per litr and the galvanometer deflexions, d, in mm.

(1) m-*Dinitrobenzene* (*Plates I and II*).—The alcoholic solutio contained 0·1 g. of *m*-dinitrobenzene in 100 c.c.; 0·1 c.c. of th solution was added from a pipette to the reaction vessel, the volum of which was 3·50 c.c. Since the molecular weight of *m*-dinitr benzene is 168, the dilution of the ammonia solution was 5880 litre In Tables VI and VII are given the results at a number of wav lengths. For the extinction coefficient measurements, t is the mea time of the exposure; when conductivity measurements were mad simultaneously, the figure given is for a time mid-way between th beginning and the end of the exposure.

In a further experiment at − 38° (Plate II) similar values of were obtained. These are not given, since there are no data for th specific conductivity of *m*-dinitrobenzene at this temperature.

(2) 2 : 4-*Dinitrotoluene*.—The change in the intensity of the ligh falling on the plate was much greater than in the experiments wit *m*-dinitrobenzene, since the reaction was followed over a greate range of concentrations. The range of exposures was so great tha the Schwarzschild relation, $D = k\,I\,T$, no longer held. It wa therefore necessary to employ another method of calibrating th photographic plate. Dilute aqueous solutions of permanganate o known concentrations (less than $M/1000$) were placed in the cel and used to determine the manner in which the intensity on th photographic plate varied with the concentration of the solution i

the path of the light. This method when employed for *m*-dinitrobenzene gave results almost identical with those obtained by the first method.

TABLE VI.

Plate I. *m*-Dinitrobenzene. Temp. = − 34·5°.

t (*mins.*).	d_t.	$10^7 . c_t$.	*k*.	d_t.	$10^7 . c_t$.	*k*.
3	81	978	0·286	12	847	0·230
6	104	1291	0·237	30	1205	0·205
9	112	1420	0·200	35	1340	0·173
15	121	1583	0·180	40	1505	0·145
20	124	1642	0·168	43	1622	0·154
25	125	1663	0·147	44	1665	0·154
30	126	1683	0·154	44	1665	0·129
	$\lambda = 4340$; $E = 202$.			$\lambda = 4560$; $E = 326$.		
3	109	971	0·283	134	1072	0·333
6	134	1312	0·246	158	1388	0·283
9	143	1471	0·223	164	1488	0·230
15	149	1591	0·184	168	1557	0·166
20	151	1635	0·163	171	1613	0·150
25	152	1658	0·147	173	1651	0·143
30	153	1682	0·152	174	1671	0·136
	$\lambda = 4192$; $E = 259$.			$\lambda = 4140$; $E = 235$.		

TABLE VII.

2 : 4-Dinitrotoluene.

Temp. = − 34°; v = 4170; λ = 4650 Å.			Temp. = − 35·1°; v = 4340; λ = 4650 Å.		
t.	$c_t . 10^7$.	*k*.	*t*.	$c_t . 10^7$.	*k*.
20	520	0·0122	20	407	0·0097
40	876	0·0113	40	773	0·0102
60	1236	0·0120	90	1342	0·0097
90	1436	0·0101	120	1534	0·0092
120	1820	0·0117	150	1748	0·0095
150	2040	0·0127	190	1919	0·0093
190	2140	0·0117	230	2064	0·0098
230	*2268*	*0·0126*	*270*	*2110*	*0·0092*
270	2240	0·0101			
300	2330	0·0150			

Summary.

The velocity of the process of ionisation of solutions of *m*-dinitro-compounds in liquid ammonia obeys a first-order law, even in those cases where the ionisation does not proceed to completion. Measurements of the change in conductivity and extinction coefficients of solutions of *m*-dinitro-compounds in liquid ammonia have shown that the ionic concentration at any time is proportional to the conductivity. The coloured ion in these solutions is an organic anion.

The most probable course of the reaction is

$$R(NO_2)_2 + 2NH_3 \overset{(I)}{\rightleftharpoons} R(NO_2)_2,2NH_3 \overset{(II)}{\rightleftharpoons} R(NO_2)_2^{--} + (N_2H_6)^{++},$$

the velocity of the reaction being governed by (I), which proceeds completion. The process of ionisation is very probably instantaneou

The temperature coefficient is that of ordinary chemical reaction *i.e.*, the velocity doubles for 10° rise of temperature; the critic increment is about 7520 cal.

No evidence has been obtained for the existence in the solid sta of complexes such as $R(NO_2)_2,xNH_3$.

One of us (H. F. G.) wishes to express his indebtedness to tl Department of Scientific and Industrial Research for a maintenan grant. Our thanks are also due to Dr. O. L. Brady for the dinitr toluene used in this investigation.

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UNIVERSITY COLLEGE, LONDON. [*Received, August 2nd*, 1928.]

CCCLXXXII.—*The Acylation of Diazomethane. Tl Effects of Variations in the Conditions on the Exte of Formation of Chloroacetophenone from Benzo Chloride.*

By WILLIAM BRADLEY and GEROLD SCHWARZENBACH.

NIERENSTEIN and his collaborators (for references, see this vc p. 1311) have described numerous cases of the formation of chlo methyl ketones in high yield as the result of the action of dia methane on various acid chlorides in ethereal solution.

In the case of *o*-nitrobenzoyl chloride, however, Dale and Niere stein (*Ber.*, 1927, **60**, 1026) found that the product was "chl nitraldin," $C_8H_6O_3NCl$, which was supposed to be the chlo derivative of a very interesting substance, $C_8H_7O_3N$, term nitraldin and obtained by Arndt and Partale (*Ber.*, 1927, **60**, 44 by the action of diazomethane on *o*-nitrobenzaldehyde. Formald hyde was formed from "chlornitraldin" under the same co ditions as from nitraldin itself. Arndt, Eistert, and Partale (*Be* 1927, **60**, 1364) were unable to reproduce the preparation of "chl nitraldin" and obtained instead a substance $C_8H_5O_3N_3$ whi they recognised as diazonitroacetophenone. Subsequently t the general nature of the reaction for the acylation of diazomethane w established by Arndt and Amende (*Ber.*, 1928, **61**, 1222) and Bradley and Robinson (this vol., pp. 1310, 1545). The conditio noted involved the addition of the acid chloride (1 mol.) to and usual solution of diazomethane (2 mols.); and these are undou best for the preparation of diazo-ketones, since the reactio

(A) and (B) occur to the almost complete exclusion of side reactions such as (C).

$$R{\cdot}COCl + CH_2N_2 = R{\cdot}CO{\cdot}CHN_2 + HCl \quad . \quad . \quad (A)$$
$$CH_2N_2 + HCl = CH_3Cl + N_2 \quad . \quad . \quad . \quad . \quad (B)$$
$$R{\cdot}CO{\cdot}CHN_2 + HCl = R{\cdot}CO{\cdot}CH_2Cl + N_2 \quad . \quad . \quad (C)$$

Maximal yields of the diazo-ketones are obtained in this manner, and if the chloro-ketone is the object of the preparation it is still best to adopt this procedure and to submit the product to the action of hydrogen chloride.

There is no evidence that the interaction of benzoyl chloride and diazomethane yields ω-chloroacetophenone directly, the small quantities that can be detected originating from diazoacetophenone by (C).

Recently, Nierenstein (*Nature*, 1928, **121**, 940) has stated that the correct procedure for the preparation of chloro-ketones in the high yields (ω-chloroacetophenone 72%, ω-chloro-2 : 4-diacetoxyacetophenone 98%) described in the literature consists in adding the diazomethane to the acid chloride rather than *vice versa*. This author is evidently of the opinion that the course of the reaction may be transformed by such a modification of the conditions. We are unable to confirm this suggestion and under all conditions diazoacetophenone is found to be the principal product of the interaction of diazomethane and benzoyl chloride. Our results are such as might be anticipated on the assumption that the reactions taking place are (A), (B), and (C). Of these, (B) is far more rapid than (C), which, however, is a facile reaction; (B) is also more rapid than (A), but not to such an extent that benzoyl chloride in excess is unable to compete effectively with hydrogen chloride for the diazomethane that enters the system.

The results may be interpreted and summarised as follows: *When diazomethane is in excess, reactions (A) and (B) greatly predominate*; the process is then represented by the equation

$$Ph{\cdot}COCl + 2CH_2N_2 = Ph{\cdot}CO{\cdot}CHN_2 + CH_3Cl + N_2.$$

When benzoyl chloride is in excess, (A) is still the primary reaction, but the relatively diminished concentration of diazomethane permits reaction (C) to occur to a small extent. If the reactants could be mixed instantaneously, or if the introduction of diazomethane were effected very slowly with vigorous stirring of the solution, it is possible that the yield of chloroacetophenone might be somewhat augmented. But under ordinary conditions of rapid addition or gradual addition during a period of 25 minutes we find that the action of diazomethane (1 mol.) on benzoyl chloride (1 mol.) gives

only 10—13% (total yield) of ω-chloroacetophenone, whilst the yield of ω-diazoacetophenone actually isolable is approximately 50%.

This yield is maintained whether the solvent is dried by phosphoric oxide or calcium chloride and whether the product is isolated after a few minutes or several hours. Heating the product previous to isolation entails loss of crystallisable diazo-ketone without increasing the proportion of chloro-ketone, and in all circumstances the failure to provide intimate admixture of the reactants leads to a reduction in the proportion of ω-chloroacetophenone.

An account of some further applications of the acylation of diazomethane is included in this communication. *p*-Nitrobenzoyl chloride and diazomethane yielded ω-diazo-*p*-nitroacetophenone, $NO_2\cdot C_6H_4\cdot CO\cdot CHN_2$ (I), and 3 : 4-diacetoxybenzoyl chloride similarly gave the corresponding diazo-ketone, $(AcO)_2C_6H_3\cdot CO\cdot CHN_2$ (II).

EXPERIMENTAL.

p-*Nitrobenzoyloxymethyl Benzyl Ketone*,

$$CH_2Ph\cdot CO\cdot CH_2\cdot O\cdot CO\cdot C_6H_4\cdot NO_2.$$

—A solution of phenylacetyl chloride (2·3 g.; b. p. 107—108°/25 mm.) in ether (10 c.c.) was added during 3—4 minutes to ethereal diazomethane (from 6·3 c.c. of nitrosomethylurethane) cooled to − 10°; the brisk evolution of nitrogen ceased after 10 minutes. The solution was kept over-night, then washed with aqueous potassium bicarbonate, dried, and evaporated in a current of air. The resulting bright yellow oil contained a small proportion of halogen but did not possess lachrymatory properties. A viscous, halogen-free oil was obtained by cooling a solution in light petroleum and this exhibited all the usual properties of diazomethyl ketones, *inter alia*, the reactions with iodine, glacial acetic and mineral acids, and the formation of an α-ketol with cold dilute aqueous-alcoholic sulphuric acid. Sudden decomposition with loss of nitrogen occurred when the substance was heated rapidly to 90—100°. A crystalline derivative was obtained by decomposition with *p*-nitrobenzoic acid, and this reaction is doubtless of general utility for the characterisation of diazo-compounds of low melting point. The crude diazoketone (0·2 g.) was boiled with a solution of *p*-nitrobenzoic acid (0·5 g.) in acetone (10 c.c.) until a portion of the cooled liquid did not evolve nitrogen on the addition of a drop of concentrated hydrochloric acid. The solvent was distilled, and the solid residue dissolved in ether and sodium carbonate solution. The washed and dried ethereal layer gave p-*nitrobenzoyloxymethyl benzyl ketone* in excellent yield (0·35 g.). Recrystallised from aqueous alcohol, this derivative formed colourless, lustrous plates, m. p. 120° (Found : C, 64·2; H, 4·3. $C_{16}H_{13}O_5N$ requires C, 64·2; H, 4·4%).

ω-Diazo-p-*nitroacetophenone* (I).—A solution of *p*-nitrobenzoyl chloride (2·8 g.) in ether (20 c.c.) was added during 4—5 minutes to ethereal diazomethane (from 6·3 c.c. of nitrosomethylurethane); a vigorous and sustained evolution of nitrogen accompanied the separation of large, pale yellow crystals of the diazo-ketone. The reaction appeared to be complete in 10—15 minutes. After 12 hours, the crystalline material was collected and washed with ether (yield, 2·1 g.; m. p. 116—117°). A further quantity (0·9 g.; m. p. 104—108°) was obtained by evaporation of the mother-liquor in a current of air, and this was easily purified by crystallisation from ethyl alcohol (Found: C, 50·4; H, 2·8. $C_8H_5O_3N_3$ requires C, 50·3; H, 2·6%). *ω-Diazo*-p-*nitroacetophenone* melts at 116—117° without immediate decomposition; the cooled melt crystallises at once, and when reheated fuses again at 116—117°. Rapid loss of nitrogen occurs at 120—125°. Exposure to direct sunlight causes rapid deepening of the colour to ochre-yellow, but no further change appears to take place. It is moderately easily soluble in organic solvents with the exception of light petroleum. It exhibits the characteristic behaviour of diazo-compounds towards iodine, acids, and alcoholic sodium hydroxide, but is in each instance less reactive than ω-diazoacetophenone and its 3 : 4-diacetoxy-, 3 : 4 : 5-tri-acetoxy-, and 3 : 5-dimethoxy-4-benzyloxy-derivatives (Bradley and Robinson, this vol., p. 1541), which are, however, in their turn less reactive than diazoacetone.

p-*Nitro*-ω-*acetoxyacetophenone*, $NO_2·C_6H_4·CO·CH_2·OAc$.—The diazo-ketone (0·88 g.) was warmed with glacial acetic acid (5 c.c.) during 25 minutes, until the nitrogen evolution appeared to be complete, and then boiled for 2 minutes. Dilution of the cooled solution with ether (20 c.c.) caused the crystallisation of the ω-acetoxy-ketone (0·51 g., m. p. 120—121°), and a further quantity (0·24 g., m. p. 120—121°) separated when the acid was neutralised with sodium carbonate. Evaporation of the ethereal layer yielded 0·06 g. (m. p. 117—119°), the remainder being recovered as an oily solid. Recrystallised twice from ethyl alcohol, p-*nitro*-ω-*acetoxy-acetophenone* was obtained in thick, pointed prisms, m. p. 121—122°, somewhat more deeply yellow than the corresponding diazo-ketone (Found: C, 53·5; H, 4·0. $C_{10}H_9O_5N$ requires C, 53·8; H, 4·1%). It is easily oxidised by warm Fehling's solution.

A substance crystallising from alcohol in small, dark-coloured needles, m. p. 132°, is described as *p*-nitro-ω-acetoxyacetophenone by Dale and Nierenstein (*Ber.*, 1927, **60**, 1026).

ω-*Diazo*-3 : 4-*diacetoxyacetophenone* (II).—Finely powdered *o*-diacetylprotocatechuic acid (10 g.) in carbon tetrachloride (15 c.c.) was converted into the chloride by warming with phosphorus

pentachloride (9·5 g.) (compare Fischer, Bergmann, and Lipschitz, *Ber.*, 1918, **51**, 55). Recrystallised from carbon tetrachloride–light petroleum, the product had m. p. 48—50° (Malkin and Nierenstein, *Ber.*, 1928, **61**, 797, give m. p. 55°).

A solution of the chloride (5 g.) in ether (75 c.c.) was cooled to 0° and added during 5 minutes to ethereal diazomethane (from 9·2 c.c. of nitrosomethylurethane) cooled to – 5°. Nitrogen was evolved and the product quickly crystallised in pale yellow, pointed prisms (yield, 3·25 g.; m. p. 75—77°). The mother-liquor was kept over-night and then concentrated in a current of air and the yellow, crystalline residue was dissolved in benzene and recovered by the addition of light petroleum to the warm solution (yield, 1·35 g.; m. p. 71—76°, and 75—77° after recrystallisation). As in previous instances, this product was already almost pure. Recrystallised twice from the same solvent, lemon-yellow, slender, rhomboidal prisms, m. p. 76—77°, were obtained. Decomposition with loss of nitrogen occurred at 103—105° (Found: C, 54·9; H, 3·8; N, 10·3. $C_{12}H_{10}O_5N_2$ requires C, 55·0; H, 3·8; N, 10·7%). *ω-Diazo-3 : 4-diacetoxyacetophenone* exhibits normal behaviour towards iodine, and acetic and mineral acids; the cold alcoholic solution becomes orange on the addition of a drop of sodium hydroxide and a flocculent precipitate slowly separates. It is easily soluble in most organic solvents with the exception of light petroleum.

A mixture of the diazo-ketone (0·5 g.) and glacial acetic acid (3 c.c.) was heated at 65—70° and then boiled for 2 minutes, and the product was isolated as in the previous example. The ω : 3 : 4-triacetoxyacetophenone crystallised from aqueous alcohol and finally from benzene–light petroleum in stout, colourless plates, m. p. 92—93°, in fair agreement with that recorded by Voswinckel (94°; *Ber.*, 1909, **42**, 4651) and by Robertson and Robinson (95°; this vol., p. 1528). It reduced Fehling's solution, slowly in the cold, rapidly on heating. When it was boiled with dilute sulphuric acid, a clear solution was obtained and this reduced Fehling's solution immediately in the cold.

ω-Chloro-3 : 4-diacetoxyacetophenone.—Finely powdered ω-diazo-3 : 4-diacetoxyacetophenone (0·7 g.) was dissolved and suspended in dry ether (50 c.c.), and dry hydrogen chloride admitted into the cold solution until decomposition was complete. Evolution of nitrogen accompanied absorption of the gas, a large excess of the latter being avoided. The solution was filtered from a small amount of flocculent material and evaporated in a current of dry air, leaving a faintly yellow, crystalline residue (0·66 g., m. p. 104—107°). Recrystallisation from benzene–light petroleum gave odourless, almost colourless tables, m. p. 107·5—108° (Found: Cl, 13·1; 13·0.

$C_{12}H_{11}O_5Cl$ requires Cl, 13·1%), in fair agreement with that recorded by Voswinckel (110°; *loc. cit.*); Malkin and Nierenstein (*loc. cit.*), however, find m. p. 94°.

This derivative was insoluble in aqueous sodium carbonate and gave no coloration with ferric chloride in alcoholic solution.

Cinnamoyl Chloride and Diazomethane.—The interaction of cinnamoyl chloride (2·5 g.) with an excess of diazomethane in ethereal solution resulted in the rapid separation of a pale yellow, crystalline substance (1·55 g.), which was unstable and became oily on keeping. It possessed the characteristic properties of a diazo-compound. Somewhat deeply yellow prisms, m. p. 77—78° (Found: N, 22·9%), were obtained by freezing a solution of this product in light petroleum, and these may have consisted mainly of the pyrazoline related to diazomethyl styryl ketone.

Benzoyl Chloride and Diazomethane.—Bradley and Robinson (*loc. cit.*) described the formation of ω-diazoacetophenone in 50% or 90% yield, according as benzoyl chloride (1 mol.) was added to 1 mol. or 2 mols. of ethereal diazomethane. The products formed when the chloride is initially in excess are now described.

Expt. 1. Ethereal diazomethane (70 c.c. containing 2·4 g. of diazomethane by titration) was added in one portion to a molecular proportion of benzoyl chloride (7·9 g.) in ether (25 c.c.) cooled to − 5°. Considerable evolution of nitrogen occurred. The bright yellow solution was kept over-night and then evaporated in a stream of dry air. The residual oil was dissolved in ether (25 c.c.) and shaken with sodium carbonate solution (70 c.c. of 10%) during 7 hours, and benzoic acid (1·06 g., corresponding to benzoyl chloride 1·25 g.) was isolated. After drying and removal of the solvent at 35—40° under reduced pressure, the unhydrolysed material was dissolved in light petroleum. Pale yellow needles of ω-diazoacetophenone (3·85 g., m. p. 45—47°) crystallised on cooling. Evaporation of the mother-liquor yielded oily material; the whole of the solvent was therefore removed and the chlorine content of the residue (2·45 g.), which contained much ω-diazoacetophenone, determined (Found: Cl, 8·6%). On the assumption that the halogen was present wholly as ω-chloroacetophenone, the yield of the latter was about 0·9 g.

Expt. 2. Ethereal diazomethane (85 c.c. containing 2·1 g. of diazomethane by titration) was added during 10 minutes and in portions of about 5 c.c. to a molecular proportion of benzoyl chloride (6·9 g.) in ether (25 c.c.), which was cooled to − 5° and vigorously shaken during the addition. One hour after the evolution of nitrogen had ceased the solution was evaporated in a current of dry air and the yellow residue, which contained much crystalline material, was

mixed with light petroleum and cooled to $-10°$. Immediate crystallisation of ω-diazoacetophenone ensued, and this was collected and washed with light petroleum. The yield was 3·7 g., m. p. 44—48°. Recrystallisation of this product from the same solvent gave pure ω-diazoacetophenone (2·85 g.). Less pure fractions were obtained by concentrating the mother-liquor, and finally, by strong cooling, colourless, crystalline material (0·05 g., m. p. 29—42°), doubtless impure ω-chloroacetophenone.

The original mother-liquor was evaporated in a current of air, *and the residue shaken with sodium carbonate (7 g.) in water (50 c.c.)* during 7 hours. The concentrated aqueous solution gave benzoic acid (1·02 g., corresponding to benzoyl chloride 1·18 g.), and no additional quantity was obtained by repetition of the sodium carbonate extraction. The unhydrolysed oil contained both ω-diazo- and ω-chloro-acetophenone; it solidified at $-15°$.

The ether employed in expts. 1 and 2 was dried by phosphoric oxide.

Expt. 3. In this case ether dried over calcium chloride was used throughout. Diazomethane (from 10·7 c.c. of nitrosomethylurethane) was distilled during 25 minutes into a solution of benzoyl chloride (6·9 g.) in ether (25 c.c.) cooled to $-10°$. The lemon-yellow crystalline residue obtained by evaporating the solvent in a current of air was mixed with light petroleum, collected, washed, and recrystallised from the same solvent (total yield, 4·5 g.; m. p. 46—49°). The oil recovered from the mother-liquor was freed from unchanged benzoyl chloride and then weighed 1·4 g. It contained ω-diazoacetophenone; a very small amount of colourless, crystalline material having the odour of ω-chloroacetophenone was precipitated on the addition of a little cold alcohol.

Expt. 4. Diazomethane (from 10·4 c.c. of nitrosomethylurethane) was distilled during 35 minutes into benzoyl chloride (8·0 g.) in ether (25 c.c.) cooled in ice. The solution was kept over-night and then concentrated to 10 c.c. by evaporation from a water-bath maintained at 50—60°. The residue, diluted with ether (10 c.c.) and shaken with sodium carbonate (7 g.) in water (70 c.c.) during 6 hours, gave benzoic acid (2·1 g., corresponding to 2·45 g. of benzoyl chloride) and a bright yellow oil which, after drying in ethereal solution, weighed 5·1 g. The oil solidified almost completely on cooling to a pale yellow, crystalline mass, which, recrystallised from light petroleum, gave ω-diazoacetophenone (2·6 g.; m. p. 42—48°, and 47—49° after further recrystallisation). The remainder of the material (2·4 g.) separated in an oily condition (Found: Cl, 6·3, 6·5%). It contained much ω-diazoacetophenone. On the assumption that the whole of the halogen was present as ω-chloroaceto-

phenone, the amount of the latter formed in the reaction and subsequent isolation was 0·67 g. (uncorrected for loss due to hydrolysis).

Expt. 5. Ethereal diazomethane (98 c.c. containing 2·54 g. of diazomethane by titration) was added during 5 minutes to a molecular proportion of benzoyl chloride (8·45 g.) in ether (25 c.c., dried by phosphoric oxide) cooled to − 5°, the apparatus having been filled previously with dry carbon dioxide. Brisk evolution of nitrogen occurred and quickly ceased; the gas was collected over concentrated sulphuric acid. After 30 minutes, the apparatus was washed out with carbon dioxide and the gases were kept in contact with the acid until absorption of ether vapour ceased (48 hours). Carbon dioxide was removed by exposure to dilute caustic soda solution; methyl chloride was presumably absent, since no further reduction in volume occurred in contact with alcohol. The final volume was 1000 c.c. at 25° and 758 mm., corresponding to 886 c.c. at N.T.P. The crude reaction product (8·15 g.) (Found : Cl, 11·3%) was isolated by evaporation of the solvent in a current of dry air, and a portion (6·50 g.) was dissolved in ether (25 c.c.) and shaken with 10% sodium carbonate solution (150 c.c.) during 14 hours. The aqueous solution then contained chlorine (0·54 g., corrected for the chlorine content of the original solution); benzoic acid (1·28 g., corresponding to benzoyl chloride 1·49 g.) was isolated by extraction of the acidified solution with ether; the unhydrolysed oil (4·48 g.) was also examined (Found : Cl, 4·1; N, 10·1, 9·9%).

The figures indicate that 1·22 g. of chlorine were lost as methyl chloride—to this correspond 770 c.c. of nitrogen (at N.T.P.)—and that 0·23 g. of chlorine was present as ω-chloroacetophenone (no account being taken of the small amount lost during hydrolysis)—the volume of nitrogen evolved during the formation of this from ω-diazoacetophenone is 145 c.c. The total calculated volume is 915 c.c., in fair agreement with that actually collected (886 c.c.). The nitrogen present as ω-diazoacetophenone would occupy 448 c.c. at N.T.P.; and the total nitrogen accounted for, 1334 c.c. The volume theoretically obtainable from the diazomethane employed is 1355 c.c. The whole of the nitrogen and chlorine present in the reactants is thus accounted for in the free nitrogen, methyl chloride, ω-diazoacetophenone, and ω-chloroacetophenone in the product.

Expt. 6. Two molecular proportions of benzoyl chloride (16·0 g.) in ether (25 c.c.) were cooled in ice while ethereal diazomethane (95 c.c. containing 2·47 g. of diazomethane by titration) was added during 5 minutes. The solution was well shaken, kept over-night, and heated at the boiling point during 1 hour. It was then divided into two equal portions and one of these was evaporated in a current of air. Hydrolysis with excess of 10% sodium carbonate solution

gave benzoic acid (3·45 g., corresponding to benzoyl chloride 4·0 g.) and a pale yellow oil which contained both ω-diazo- and ω-chloro-acetophenone. The amount of the latter was considerably greater than the normal yield in experiments involving only one molecular proportion of benzoyl chloride.

Expt. 7. In a second similar experiment, diazomethane (from ·2 c.c. of nitrosomethylurethane) was distilled during 25 minutes into benzoyl chloride (8·0 g.) in ether (25 c.c.) cooled to − 5°. Thirty minutes after the distillation was complete the product was washed with standard potassium bicarbonate solution; only very little more hydrogen chloride was extracted than from a similar blank experiment with ethereal benzoyl chloride. Isolated and hydrolysed in the usual manner, the product gave benzoic acid (3·7 g., corresponding to benzoyl chloride 4·3 g.). The greater portion of the unhydrolysed material was crystalline and contained much ω-diazo-acetophenone; very little ω-chloroacetophenone was present.

The technique involved in the above procedure was critically examined and doubtless gives a substantially correct estimate of the composition of the reaction product. (a) Benzoyl chloride (4 g.) in ether (70 c.c.) was hydrolysed, and benzoic acid (3·2 g.) isolated (theory requires 3·5 g.). (b) Hydrolysis of ω-chloroacetophenone occurred only to a small extent. Estimation of the amount of hydrogen chloride formed by shaking ω-chloroacetophenone (1·0 g., ·4 g., and 3·4 g.) in ether (25 c.c.) with 10% sodium carbonate solution (100 c.c., 150 c.c., and 150 c.c.) during (7 hours, 7 hours, and 4 hours) showed that (0·13 g., 0·33 g., and 0·52 g.) of the chloro-ketone had been hydrolysed. (c) The yield of diazomethane from nitrosomethylurethane varied between relatively small limits. In titration experiments, nitrosomethylurethane (12·6 c.c., 25·2 c.c., 2·6 c.c., and 12·6 c.c.) gave diazomethane (2·4 g., 5·1 g., 2·8 g., and 8 g.). The yields calculated according to Houben-Weyl ("Die Methoden der Organischen Chemie," 1923, 3, 124) are 2·4 g., 4·8 g., ·4 g., and 2·4 g., respectively.

The correct interpretation of the course of the reaction between acid halides and diazomethane was suggested to us by Professor R. Robinson, F.R.S., whom we thank for his interest in the above experiments.

THE UNIVERSITY, MANCHESTER. [Received, August 1st, 1928.]

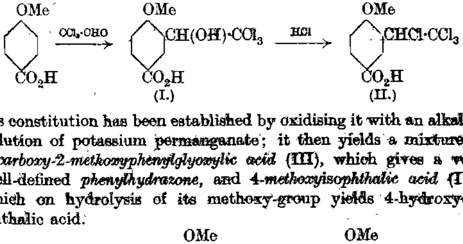
CCCLXXXIII.—*The Condensation of Chloral with Anisic Acid, with* p-*Nitroanisole, and with* 2 : 6-*Dichloroquinol.*

By Frederick Daniel Chattaway and Fernando Calvet.

Many phenols substituted in the para-position readily condense with chloral under the influence of concentrated sulphuric acid and form derivatives of 1 : 3-benzdioxin (Chattaway, J., 1926, 2720; Chattaway and Calvet, J., 1927, 685; this vol., p. 1088; Chattaway and Morris, J., 1927, 2083).

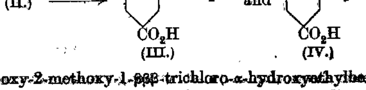
When, however, the formation of the heterocyclic benzdioxin ring is prevented by replacement of the phenolic hydroxyl by an alkyloxy-group, only one molecule of chloral reacts and a single βββ-trichloro-α-hydroxyethyl group, $\cdot CH(OH)\cdot CCl_3$, is introduced into the nucleus in a position ortho to the alkyloxy-group. For example, anisic acid condenses thus to form *5-carboxy-2-methoxy-1-βββ-trichloro-α-hydroxyethylbenzene* (I).

This compound can be isolated during the first stages of the action. If, however, this be prolonged for many days, hydrogen chloride, which is slowly produced by the decomposition of some small amount of the chloral, replaces the α-hydroxyl group by a chlorine atom and the final product is *5-carboxy-2-methoxy-1-αβββ-tetrachloroethylbenzene* (II).



(I.) (II.)

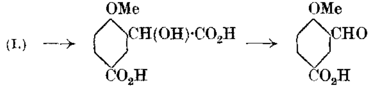
Its constitution has been established by oxidising it with an alkaline solution of potassium permanganate; it then yields a mixture of *5-carboxy-2-methoxyphenylglyoxylic acid* (III), which gives a very well-defined *phenylhydrazone*, and *4-methoxyisophthalic acid* (IV), which on hydrolysis of its methoxy-group yields 4-hydroxy*iso*phthalic acid.



(III.) (IV.)

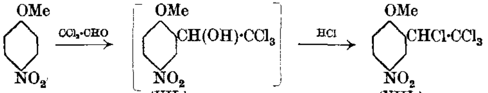
5-Carboxy-2-methoxy-1-βββ-trichloro-α-hydroxyethylbenzene (I), which melts about 73° higher than the corresponding 2-ethoxy-

derivative (Chattaway and Calvet, J., 1927, 689), is a comparativel stable substance, the methoxy-group not being easily hydrolysec When the substance is heated with concentrated sulphuric acid on water-bath, hydrogen chloride is liberated and 4-*methoxyisophtha aldehydic acid* (VI) is formed, probably by elimination of formic aci from the 5-carboxy-2-methoxymandelic acid (V) which must be th first product of the hydrolysis.



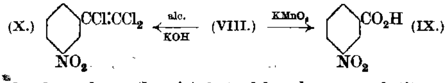
(V.) (VI.)

p-Nitroanisole condenses with chloral in a similar manner i presence of concentrated sulphuric acid. When the action is pro longed, 5-*nitro-2-methoxy*-1-αβββ-*tetrachloroethylbenzene* is forme (VIII). The intermediate product of the action, 5-nitro-2-methoxy 1-βββ-trichloro-α-hydroxyethylbenzene (VII), has not actuall been isolated; but its formation is certain, since when the solutio of *p*-nitroanisole and chloral in concentrated sulphuric acid is satu ated at the beginning with hydrogen chloride the final product i formed much more rapidly and completely than when the necessar hydrogen chloride is formed by the comparatively slow decomposi tion of the chloral.



(VII.) (VIII.)

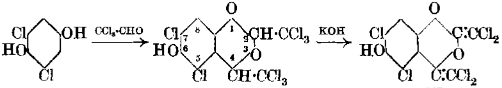
The constitution of the final condensation product was establishe by oxidising it with potassium permanganate in acetone solution it then yielded 5-nitro-2-methoxybenzoic acid (IX), identical wit the product obtained by nitration of *o*-methoxybenzoic acid. Whe acted upon by boiling alcoholic potash, it lost one molecule o hydrogen chloride and yielded αββ-*trichloro-5-nitro-2-methoxystyren* (X).



It has been shown (*loc. cit.*) that, although many substituents i a position ortho to the phenolic hydroxyl hinder the formation of

benzdioxin ring, they have little or no effect when in a meta-position. Condensation also proceeds in the usual manner when both meta-positions are thus occupied. For example, 2 : 6-dichloroquinol, in which both positions meta to one of the two hydroxyls are occupied by chlorine atoms, condenses readily, under the influence of concentrated sulphuric acid, with two molecules of chloral, yielding 5 : *7-dichloro-6-hydroxy-2 : 4-bistrichloromethyl-1 : 3-benzdioxin* (XI), only the hydroxyl group which has both the adjacent *o*-positions unoccupied taking an active part in the reaction.

The heterocyclic dioxin ring of this condensation product shows unusual resistance to the action of alcoholic potash, which only removes a molecule of hydrogen chloride from each of the side chains and forms 5 : *7-dichloro-6-hydroxy-2 : 4-bisdichloromethylene-1 : 3-benzdioxin* (XII).



(XI.) (XII.)

The benzdioxin ring in 6-amino-2 : 4-bistrichloromethyl-1 : 3-benzdioxin behaves similarly (see this vol., p. 1089).

EXPERIMENTAL.

5-Carboxy-2-methoxy-1-βββ-trichloro-α-hydroxyethylbenzene (I).—A solution of 40 g. (1 mol.) of anisic acid and 50 g. (1·2 mols.) of chloral hydrate in 400 c.c. of concentrated sulphuric acid was kept at the ordinary temperature for 10 hours and then poured into 2000 c.c. of water containing ice. A viscid mass separated which, after being heated with water, broke up into a mass of needle-shaped crystals; these were recrystallised from alcohol and from chloroform-light petroleum. *5-Carboxy-2-methoxy-1-βββ-trichloro-α-hydroxyethylbenzene* is sparingly soluble in benzene and chloroform, practically insoluble in light petroleum, and easily soluble in boiling acetic acid and alcohol, from which it slowly separates as highly refractive, short prisms, m. p. 198—199° (Found: C, 39·9; H, 3·2; Cl, 35·8. $C_{10}H_9O_4Cl_3$ requires C, 40·1; H, 3·0; Cl, 35·6%).

5-Carboxy-2-methoxy-1-αβββ-tetrachloroethylbenzene (II).—(1) *By condensation of anisic acid and chloral in presence of concentrated sulphuric acid.* A solution of 50 g. of anisic acid and 60 g. of chloral hydrate in 500 c.c. of concentrated sulphuric acid was kept at the ordinary temperature for 8 days, hydrogen chloride being gradually formed in considerable quantity. When the clear resulting liquid was poured into 3000 c.c. of water *5-carboxy-2-methoxy-1-αβββ-tetra-*

chloroethylbenzene separated as a voluminous white solid; this, after being washed with hot water, crystallised from alcohol in colourless needles (50 g.), m. p. 247—249° (Found: C, 37·85; H, 2·45; Cl, 44·65; *M*, 331. $C_{10}H_8O_3Cl_4$ requires C, 37·8; H, 2·5; Cl, 44·7%; *M*, 318). The substance is sparingly soluble in boiling water, moderately easily soluble in boiling benzene, chloroform, and light petroleum, and easily soluble in boiling alcohol and in aqueous alkalis.

(2) *By the action of hydrogen chloride upon 5-carboxy-2-methoxy-1-βββ-trichloro-α hydroxyethylbenzene.* A solution of 2 g. of the trichloro-compound in 20 c.c. of concentrated sulphuric acid was saturated with dry hydrogen chloride, kept at the ordinary temperature for 1 day, and then poured into 50 c.c. of water containing ice. The solid which separated was recrystallised from alcohol; it melted at 247—249° and was identical in every respect with the substance described in (1).

Action of Concentrated Sulphuric Acid on 5-Carboxy-2-methoxy-1-βββ-trichloro-α-hydroxyethylbenzene.—A solution of 10 g. of the trichloro-compound in 100 c.c. of concentrated sulphuric acid was heated on a water-bath for 45 minutes until hydrogen chloride ceased to be evolved. It was then cooled and poured into 500 c.c. of water containing ice. The *4-methoxy*iso*phthalaldehydic acid* (VI) that separated (yield, 4·5 g.) crystallised from alcohol in very small, colourless plates, m. p. 244—245° (Found: C, 59·5; H, 4·7. $C_9H_8O_4$ requires C, 60·1; H, 4·45%). When heated with 2 : 4-dichlorophenylhydrazine it yielded the 2 : 4-*dichlorophenylhydrazone*, which crystallised from alcohol in very small, pale yellow needles, m. p. 303—305° (decomp.) (Found: Cl, 20·85. $C_{15}H_{12}O_3N_2Cl_2$ requires Cl, 20·9%).

*Oxidation of 5-Carboxy-2-methoxy-1-αβββ-tetrachloroethylbenzene. Isolation of 4-Methoxy*iso*phthalic Acid* (IV) *and 5-Carboxy-2-methoxyphenylglyoxylic Acid* (III).—5-Carboxy-2-methoxy-1-αβββ-tetrachloroethylbenzene (15 g.) was dissolved in 300 c.c. of boiling water containing an excess of sodium carbonate, and about 30 g. of finely powdered potassium permanganate were added gradually until it was no longer decolorised on continued boiling. The manganese dioxide was filtered off, and the colourless filtrate made acid with hydrochloric acid; *4-methoxy*iso*phthalic acid* (4·5 g.) then separated. It was several times recrystallised successively from acetic acid, dilute alcohol, and finally from boiling water, from which it separated in minute colourless needles, m. p. 275—276° (Found: C, 55·0; H, 4·3. $C_9H_8O_5$ requires C, 55·1; H, 4·1%).

When heated for 5—10 minutes with hydriodic acid (b. p. 127°), it gave 4-hydroxy*iso*phthalic acid, m. p. 310°.

The aqueous acid mother-liquor from which the 4-methoxy*iso*-phthalic acid had separated was repeatedly extracted with ether. Evaporation of the ether left 5-*carboxy-2-methoxyphenylglyoxylic acid* as a crystalline, colourless solid; this was easily soluble in boiling acetic acid, from which it separated in small colourless prisms, m. p. 254—255° (Found: C, 53·3; H, 3·8. $C_{10}H_8O_6$ requires C, 53·6; H, 3·6%).

It reacts with hydrazines to form sparingly soluble hydrazones. The *phenylhydrazone* separates from boiling alcohol in pale yellow, microscopic prisms, m. p. 231° (decomp.) (Found: C, 61·0; H, 4·6; N, 8·9. $C_{16}H_{14}O_5N_2$ requires C, 61·2; H, 4·5; N, 8·9%).

5-*Nitro-2-methoxy-1-αβββ-tetrachloroethylbenzene* (VIII).—A solution of 50 g. of *p*-nitroanisole (1 mol.) and 60 g. of chloral hydrate (1·1 mols.) in 450 c.c. of concentrated sulphuric acid was kept at the ordinary temperature, hydrogen chloride being slowly liberated. Crystals of 5-*nitro-2-methoxy-1-αβββ-tetrachloroethylbenzene*, which began to appear after 10 to 12 days, were separated after 4 weeks, well washed with water, and recrystallised from alcohol (yield, 33 g.). The substance is insoluble in water, very sparingly soluble in light petroleum, and easily soluble in boiling acetone, benzene, and alcohol, from which it separates in slightly yellow needles, m. p. 131—132° (Found: N, 4·4; Cl, 44·4; *M*, cryoscopic in benzene, 340. $C_9H_7O_3NCl_4$ requires N, 4·4; Cl, 44·5%; *M*, 319).

When the condensation of chloral with *p*-nitroanisole was carried out in concentrated sulphuric acid saturated with hydrogen chloride, separation of the product began on the third day and was practically complete by the eighth day.

Action of Potassium Hydroxide on 5-*Nitro-2-methoxy-1-αβββ-tetrachloroethylbenzene: Formation of αββ-Trichloro-5-nitro-2-methoxystyrene* (X).—The tetrachloro-compound (2 g.) was heated for a short time with 25 c.c. of a mixture of equal parts of alcohol and a 50% aqueous solution of potassium hydroxide. As the reaction proceeded, αββ-*trichloro-5-nitro-2-methoxystyrene* separated as an oil, which solidified on cooling and then crystallised from alcohol in pale yellow, shining plates, m. p. 94—95° (Found: N, 4·9; Cl, 37·6. $C_9H_6O_3NCl_3$ requires N, 4·95; Cl, 37·7%).

Oxidation of 5-Nitro-2-methoxy-1-αβββ-tetrachloroethylbenzene to 5-Nitro-2-methoxybenzoic Acid (IX).—Potassium permanganate (30 g.) was added during 48 hours to 5 g. of 5-nitro-2-methoxy-1-αβββ-tetrachloroethylbenzene dissolved in 100 c.c. of boiling acetone. After 48 hours' boiling, the solid formed was separated from the cooled liquid and extracted with 100 c.c. of alcohol. Partial evaporation of the extract gave needles of potassium 5-nitro-2-methoxybenzoate, from which the acid, m. p. 161°, was obtained (Found:

C, 48·85; H, 3·4; N, 7·7. Calc. for $C_8H_7O_5N$: C, 48·7; H, 3·5 N, 7·1%), identical with a specimen prepared by the method c Simonsen and Rau (J., 1917, **111**, 228).

5:7-*Dichloro-6-hydroxy-2:4-bistrichloromethyl-1:3-benzdioxin* (XI —To a solution in 250 c.c. of concentrated sulphuric acid of 25 g (1 mol.) of 2:6-dichloroquinol, obtained by oxidising 2:4:6 trichlorophenol with cold fuming nitric acid and reducing the 2:6 dichlorobenzoquinone formed by sulphur dioxide, 48 g. of chlora hydrate were added. The mixture was well shaken for ½ hour an kept for 3 days at the ordinary temperature. Ice was then adde and 5:7-*dichloro-6-hydroxy-2:4-bistrichloromethyl-1:3-benzdioxin* which separated as a viscid, colourless mass, was well washed wit water and repeatedly crystallised from alcohol (yield, 41 g.). I was easily soluble in boiling alcohol, chloroform, and benzene an sparingly soluble in light petroleum and separated from these solvent in small, glistening, colourless plates, m. p. 114—115° (Found C, 26·15; H, 1·0; Cl, 62·1. $C_{10}H_4O_3Cl_8$ requires C, 26·05; H, 0·85 Cl, 62·2%). It dissolved in aqueous alkalis and gave a greenish brown colour with a solution of ferric chloride.

The phenolic hydroxyl group is easily acetylated when the com pound is heated for a short time with acetyl chloride or aceti anhydride containing a drop of sulphuric acid. 5:7-*Dichloro-6 acetoxy-2:4-bistrichloromethyl-1:3-benzdioxin* crystallises from boil ing alcohol, in which it is moderately easily soluble, in small, colour less prisms, m. p. 179—180° (Found: Cl, 57·2. $C_{12}H_6O_4Cl_8$ require Cl, 57·0%).

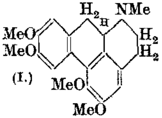
5:7-*Dichloro-6-hydroxy-2:4-bisdichloromethylene-1:3-benzdioxin* (XII).—To a boiling solution of 5 g. of potassium hydroxide (9 mols. in 50 c.c. of alcohol, 4·5 g. of 5:7-dichloro-6-hydroxy-2:4-bistrichloro methyl-1:3-benzdioxin (1 mol.) were added and the mixture wa boiled under reflux for 15 minutes; 50 c.c. of hot water were then added and the alcohol was distilled off in a current of steam. From the cooled, acidified liquid, 5:7-*dichloro-6-hydroxy-2:4-bisdichloro methylene-1:3-benzdioxin* separated. It is easily soluble in boiling alcohol, chloroform, and carbon tetrachloride, from which it separate in small, compact, colourless crystals, m. p. 137—138° (Found Cl, 55·5. $C_{10}H_2O_3Cl_6$ requires Cl, 55·6%). When dissolved in carbo tetrachloride, it does not combine with bromine at the ordinary temperature.

THE QUEEN'S COLLEGE, OXFORD. [*Received, August 30th*, 1928.]

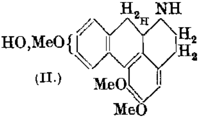
CCCLXXXIV.—*The Constitution of Laurotetanine.*

By George Barger and Robert Silberschmidt.

LAUROTETANINE is an alkaloid discovered by Greshoff ("Verslag h. onderzoek v.d. Plantenstoffen Ned. Indie," 1890, 98; *Ber.*, 90, **23**, 3537) in various *Lauraceæ;* injected, it causes tetanic nvulsions. It was studied by Filippo (*Arch. Pharm.*, 1898, 6, 601) and particularly by Gorter (*Bull. Jard. bot. Buitenzorg,* 21, **3**, 180). The latter showed that the anhydrous base is $_{6}H_{10}(OH)(NH)(OMe)_3$ and being impressed by the chemical and ysiological resemblance of its *N*-methyl methyl ether to the kaloid glaucine, he assumed the same carbon skeleton in both kaloids. Now glaucine (I) has been synthesised from laudanosine Gadamer (*Arch. Pharm.*, 1911, **249**, 680) and is a derivative of enanthrenc and *iso*quinoline. Since Gorter regarded the *N*-methyl



(I.)



(II.)

ethyl ether of laurotetanine as different from glaucine, he named *iso*glaucine and considered the isomerism due to different positions two methoxy-groups. A further study of these compounds and e products of their exhaustive methylation by Hofmann's method s, however, convinced us that glaucine and Gorter's "*iso*glaucine" e identical, so that laurotetanine may be represented by (II).

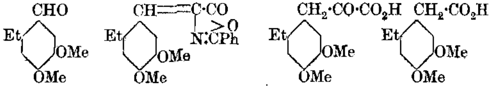
The one free hydroxyl group is as indicated in the benzene ring tached to two carbon atoms, for on oxidation of laurotetanine orter found that the benzene ring attached to three carbon atoms rvives as a dimethoxybenzenetricarboxylic acid. The choice tween the two possible formulæ indicated by (II) might perhaps made by exhaustive methylation of laurotetanine ethyl ether d comparison of the product with two synthetic ethoxytri-ethoxyethylphenanthrenes.

We carried out a number of preliminary experiments with this d in view. Although we could readily obtain from laurotetanine d glaucine a vinylphenanthrene and a phenanthrenecarboxylic id, we were quite unable to decarboxylate the acid. We therefore cided to reduce the vinyl to the ethyl compound and attempt the nthesis of the latter.

For this purpose the required 3 : 4-*dimethoxyethylbenzene* was

obtained both by reducing 3 : 4-dimethoxyvinylbenzene (from 3 : 4-dimethoxyphenylethylcarbinol by Klages' method, *Ber.*, 1903, **36**, 3588) and by reducing acetoveratrone according to Clemmensen (*Ber.*, 1913, **46**, 1838). The latter alternative avoids the complications due to the polymerisation of the vinyl compound and is much the better method. Acetoveratrone was prepared by oxidation of the phenylmethylcarbinol as well as directly from veratrole: the latter route is the cheaper.

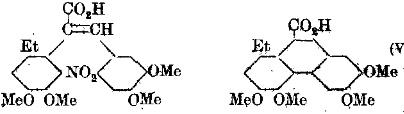
The dimethoxyethylbenzene was converted by Gattermann's reaction into an *aldehyde*, presumably (III), but this constitution has not been proved rigorously.



(III.) (IV.) (V.) (VI.)

By condensation with hippuric acid to the *azlactone* (IV), hydrolysis to the *pyruvic acid* (V), and oxidation, a *dimethoxyethylphenylacetic acid* (VI) was obtained (compare Kropp and Decker, *Ber.*, 1909, **42**, 1184; Cain, Simonsen, and Smith, J., 1913, **103**, 1036; Haworth, Perkin, and Rankin, J., 1924, **125**, 1686). This was condensed with 6-nitro-3 : 4-dimethoxybenzaldehyde to the *nitro-acid* (VII), which after reduction and diazotisation was expected to yield a *phenanthrenecarboxylic acid* (VIII). The product of the decarboxylation

(VII.)



(VIII.)

of (VIII) was very similar to that obtained by the degradation of laurotetanine, but did not appear to be identical with it. Further work will be necessary to clear up this discrepancy.

EXPERIMENTAL.

A. *Exhaustive Methylation of Laurotetanine.*

Like Gorter, we prepared the alkaloid from the bark of *Litsea citrata* from Java, using, however, a different process from the usual Stas–Otto method employed by Gorter and by Filippo, for by extraction of an alkaline solution with immiscible solvents we obtained hardly any crystalline alkaloid. An alcoholic extract prepared for us by Messrs. Duncan, Flockhart and Co. of Edinburgh was a thick, tarry mass representing about 10% by weight of the

bark. We dissolved it in two-thirds of its weight of hot glacial acetic acid, poured the solution into 5—6 volumes of water with vigorous mechanical stirring, and filtered off a precipitate (A). The brown filtrate, on being made slightly acid to litmus by addition of ammonia, gave a precipitate (B), partly composed of a weak base which probably contained several free hydroxyl groups and was readily oxidised. This alkaloid, which has some properties in common with boldine, a dihydroxydimethoxyphenanthrene alkaloid occurring in *Peumus Boldus* (*Monimiaceæ*, related to *Lauraceæ*), could not be crystallised. To the filtrate from (B) we added excess of ammonia and obtained a voluminous, pale yellow precipitate of crude laurotetanine, which was washed free from ammonia and dried on a porous tile in a vacuum. Precipitate (A) was redissolved in glacial acetic acid and treated as before, whereby it yielded a further quantity of crude laurotetanine. The dried alkaloid was powdered, mixed with sand, and extracted with ether for several days in a Soxhlet apparatus. Crystalline material soon began to separate from the ether, in which it is very sparingly soluble. It was recrystallised from acetone by the addition of a few drops of water. The hydrated alkaloid melted in its water of crystallisation at 124—134° (Gorter gives 125°; Filippo, 134°). It did not darken on exposure to light as stated by Gorter (at Buitenzorg). Yield, 0·3—0·4% (Gorter obtained 0·38%).

Complete Methylation. Dimethyl-laurotetanine Methiodide, $C_{22}H_{28}O_4NI$.—Preliminary experiments, in which laurotetanine and methyl iodide were heated in methyl-alcoholic sodium hydroxide, yielded two crystalline iodides, ultimately identified as the methiodide and methine hydriodide, but as the yield was unsatisfactory, diazomethane was used for the first step. Laurotetanine (1 g.) in 10 c.c. of methyl alcohol was mixed with an ethereal solution of diazomethane from 7 c.c. of nitrosomethylurethane. Next day, after evaporation, the methyl ether was separated by means of sodium hydroxide and treated as syrup with excess of methyl iodide in methyl alcohol. The methiodide, obtained in a yield of 60%, formed bundles of colourless needles, m. p. 210°, the same as that recorded for glaucine methiodide; the melting point remained constant on recrystallisation and did not rise to 226°, that given by Gorter for "*iso*glaucine methiodide." The methiodide was very sparingly soluble in water and could be completely extracted from aqueous solution by chloroform.

Dimethyl-laurotetaninemethine, $C_{22}H_{27}O_4N$.—The methiodide (0·5 g.) was heated for 5 hours with 40 c.c. of 10% alcoholic potassium hydroxide. The solution, which became slightly red, was concentrated and water was added; an oily base then separated.

When this was neutralised with acid, the *hydriodide* of the methine separated in colourless, rhomb-shaped leaflets, m. p. 265°, almost insoluble in water and in alcohol (Found : I, 26·2. $C_{22}H_{27}O_4N,HI$ requires I, 25·6%). The free methine, isolated after addition of ammonia and extraction with ether, could not be crystallised, and remained oily after distillation at 200° in a high vacuum. Yield, 0·4 g. The methine tenaciously retained a small quantity of an impurity, which gave it a pink colour and was less soluble in hot water than in cold. This impurity was absent from the methine prepared from glaucine, which could be obtained in colourless needles, m. p. 76°, from the dry ethereal solution, and probably accounts for the somewhat lower melting points of Gorter's "*iso*-glaucine" salts, as compared with those of glaucine.

Dimethyl-laurotetaninemethine methiodide, $C_{23}H_{30}O_4NI$, obtained on mixing the components in ethereal solution, formed white needles, m. p. 276°, very sparingly soluble in hot water.

2 : 3 : 5 : 6 - *Tetramethoxy* - 8 - *vinylphenanthrene.* — The methine methiodide (0·37 g.; 0·75 millimol.) was heated with 40 c.c. of 10% methyl-alcoholic potassium hydroxide on the water-bath, the trimethylamine evolved being swept into 0·1*N*-hydrochloric acid. After 6 hours, 6·5 c.c. of the acid (= 90% of the theoretical) had been neutralised. (The trimethylamine was isolated as the chloroplatinate, m. p. 253° after crystallising from alcohol. Found : Pt, 37·2. Calc., 36·7%.) When the solution was concentrated, crystals separated; the quantity was increased by addition of water and neutralisation. On extraction with ether and crystallisation from alcohol, slightly pink, rhomb-shaped plates, m. p. 142°, were obtained. They decolorised potassium permanganate in cold acetone. Yield, 60% (Found: C, 74·05, 74·0; H, 6·3, 6·4. $C_{20}H_{20}O_4$ requires C, 74·0; H, 6·2%).

2 : 3 : 5 : 6-*Tetramethoxyphenanthrene*-8-*carboxylic Acid*.—To a cold solution of 5·1 g. of the vinyl compound in 10 c.c. of acetone, 0·175 g. of potassium permanganate (= 5O) was added during 1 hour. The manganese dioxide was filtered off and reduced with bisulphite and the solution was added to the residue left on evaporation of the acetone filtrate. Ether extracted from the alkaline solution a little unchanged vinyl compound and then, after acidification, a substance which crystallised from acetone–water or benzene–ligroin in yellow needles, m. p. 215°, very soluble in ether (Found : equiv., by back titration, 339. $C_{19}H_{18}O_6$ requires equiv., 342).

B. *Exhaustive Methylation of Glaucine.*

The above degradation had not been carried out by Gadamer (*loc. cit.*), who deduced the constitution by converting laudanosine

into glaucine. We isolated the latter alkaloid from 10 kg. of leaves and pods of *Glaucium luteum* from the Royal Botanic Gardens, Edinburgh, and from the coast near Cockburnspath. Fischer's method (*Arch. Pharm.*, 1901, **239**, 426) was greatly simplified by utilising the minute solubility of glaucine hydriodide in the presence of potassium iodide, the glaucine salt being under these conditions almost as sparingly soluble as the precipitate with Mayer's reagent (limit at 1 : 10,000). The material was covered with water, heated to boiling, strained, passed through a mincer, stirred for 2—3 hours in the original solution after addition of 2% acetic acid, strained, and extracted a second time. The filtered extracts were concentrated in a vacuum to a half-syrupy consistency and filtered through glass wool. Potassium iodide was then dissolved in the solution; after 2 days, a layer of brownish crystals had separated. One recrystallisation from much alcohol gave long, silky needles, still slightly pink, m. p. 243° (yield, 0·2% of the fresh leaves and pods). Thus this alkaloid is readily accessible. The filtrate from the crystals gave with ammonia a small precipitate yielding the colour reactions of protopine (Fischer, *loc. cit.*).

To obtain the pure base, the iodide was shaken with aqueous ammonia and ether. The former retained the colouring matter and the latter left on evaporation colourless prisms, m. p. 118—119°, after several crystallisations.

We prepared glaucine methiodide, the methine, methine methiodide, the vinylphenanthrene, and the carboxylic acid. We also prepared the characteristic iodide of dimethyl-laurotetanine (from laurotetanine and diazomethane). We thus had six different compounds, each obtained from two natural sources. In all cases they were identical; these results, tabulated below, dispose of Gorter's alleged difference between glaucine and dimethyl-laurotetanine. We have also tabulated the melting points given by Warnat (*Ber.*, 1925, **58**, 2768) for mixtures of derivatives of dimethylboldine and glaucine. Warnat was the first to publish the Hofmann degradation of glaucine, after we had already carried it out independently.

	Dimethyl-lauro-tetanine alone.	Glaucine alone.	Glaucine + dimethyl-lauro-tetanine.	Glaucine + dimethyl-boldine.
Hydriodide	243°	243°	243°	239—241°
Methiodide	219	219	219	221
Methine hydriodide	264	264	263	—
Methine methiodide	276	278	276	276—278
Vinylphenanthrene	142	142	142	142—143
Phenanthrene acid	215	214	214	—

Having established this identity, we carried out some experiments

as first steps in the determination of the position of the fr hydroxyl in laurotetanine. In order to have a tetramethox compound which could be synthesised, we attempted to decarbox ate the tetramethoxyphenanthrenecarboxylic acid. We entir failed to do this, whether by distillation (when the acid sublim at a high temperature), or by heating with lime, or by heating glacial acetic acid. We therefore decided to base the comparis on the ethyl compound.

2 : 3 : 5 : 6-Tetramethoxy-8-ethylphenanthrene was prepared reducing 0·485 g. (1·5 millimols.) of the vinyl compound (fr glaucine), dissolved in the minimum amount of glacial acetic ac which coloured the solution red, with hydrogen after addition palladium chloride and gum arabic. The reaction stopped abrupt after 20 minutes, when 35 c.c. of hydrogen had been taken u The solution was diluted with water, and the resulting mixtu extracted with ether. The extract crystallised from meth alcohol. Yield, 80%. The crystals were distilled in a high vacuu with the bath at 200°. The colourless distillate crystallised fro alcohol in narrow plates, m. p. 120°.

Synthesis of 2 : 3 : 5 : 6-*Tetramethoxy*-8-*ethylphenanthrene.*

As we required large quantities of methyl vanillin and of veratro we paid some attention to the methylation of vanillin and guaiacol, finally obtaining a practically quantitative yield by rapid method.

Vanillin (152 g.; 1 mol.) is melted in a wide-mouthed bott provided with a condenser, a stirrer, and two tap-funnels. Wi rapid stirring, 1·5 mols. (82 g.) of potassium hydroxide in 120 c. of water are run in at the rate of two drops a second, and 20 secon after this has started, addition of 1·25 mols. (160 c.c.) of meth sulphate is begun at the same rate. (The methyl sulphate h stood over potassium carbonate and is neutral to Congo.) Th external heating is soon stopped. The reaction mixture keeps pale reddish-brown and alkaline; green indicates an acid reactio When three-quarters of the reagents have been added, the reacti mixture becomes turbid and separates into two layers. As soon all has been run in (about 20 minutes from the start) the reacti mixture is poured into a porcelain basin. The upper layer solidifi to a hard, white mass of practically pure methyl vanillin, m. p. 43 It is washed with water and dried. Yield, 165 g., or more than 99% Veratrole was similarly obtained in a yield of 95% (after extracti with ether and distillation). Pure, crystalline guaiacol must b used. Acetoveratrone was obtained from veratrole and acet chloride by means of aluminium chloride in carbon disulphi

solution in a yield of 80% and was then reduced by Clemmensen's method (*Ber.*, 1913, **46**, 1838).

3 : 4-*Dimethoxyethylbenzene*.—720 G. of zinc, amalgamated for 1 hour with double the weight of 5% aqueous mercuric chloride solution, was washed and covered with 10% hydrochloric acid. The liquid was heated to boiling and 180 g. of acetoveratrone were added in the course of an hour. The boiling was continued for 5 hours, 50—100 c.c. of acid being added per hour. The oily layer removed by ether distilled mostly at 110—112°/9 mm.; the boiling point then suddenly rose to 230—240° and a polymeride distilled. Thus the lower fraction was at once pure and stable to permanganate. Yield, 68%. The substance could not be crystallised.

3 : 4-*Dimethoxy-6-ethylbenzaldehyde* (III).—To 54 g. of dimethoxyethylbenzene in 75 g. of anhydrous benzene, cooled by ice, 60 g. of freshly powdered aluminium chloride were slowly added, then 55 g. of hydrogen cyanide. Hydrogen chloride was passed for 3 hours at 0° and for ½ hour at 30°. Next day the imide was poured on ice and finally decomposed by a current of steam. The *aldehyde* distilled at 150—159°/9 mm. and crystallised on long standing in plates, m. p. 28—30°, very soluble in organic solvents (Found: C, 67·7; H, 7·2. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·3%). The semicarbazone formed colourless crystals, m. p. 197—199°.

3 : 4-*Dimethoxy-6-ethylbenzoic acid*, prepared by oxidising the aldehyde with alkaline permanganate, had m. p. 138° (Found: equiv., 210·5. $C_{11}H_{14}O_4$ requires equiv., 210).

Azlactone of 3 : 4-*Dimethoxy-6-ethylbenzylidenehippuric Acid* (IV). —A mixture of 39 g. of the aldehyde, 40 g. of hippuric acid, 82 c.c. of acetic anhydride, and 16 g. of sodium acetate was heated for 40 minutes on the water-bath. After cooling, the semi-solid mass was washed with much ether and with water; it then separated from hot alcohol, in which it was rather sparingly soluble, in yellow crystals, m. p. 155°. Yield, 66% (Found: C, 71·0; H, 6·0. $C_{20}H_{19}O_4N$ requires C, 71·2; H, 6·0%). The acid itself, m. p. 212°, was made by heating the lactone with 1% potassium hydroxide solution until it was colourless.

3 : 4-*Dimethoxy-6-ethylphenylpyruvic Acid* (V).—20 G. of the azlactone were boiled with 30 g. of potassium hydroxide in 100 c.c. of water, the ammonia evolved being swept into *N*-acid. In 1 hour 53 c.c. had been neutralised (= 94% of the theoretical). The solution was acidified with sulphur dioxide, and the benzoic acid filtered off. The solution, which contained the pyruvic acid as bisulphite compound, was acidified with hydrochloric acid and heated under reduced pressure to remove sulphur dioxide. A crystalline precipitate separated. Recrystallised from glacial

acetic acid and from alcohol, it formed pale yellow crystals, m. · 181°; *yield*, 71%.

3 : 4-*Dimethoxy*-6-*ethylphenylacetic Acid* (VI).—The keto-aci (10 g.) in a large excess of dilute sodium hydroxide solution wa oxidised at 0° by 37 c.c. of 3% hydrogen peroxide. After neutra isation with sulphur dioxide (to keep the unchanged acid in solutio the oxidation product separated as an oil which solidified next da and was extracted with ether. It formed slightly pink bundles c needles, m. p. 67°; yield, 78% (Found : equiv., 222·5. $C_{12}H_{16}$C requires *equiv.*, 224).

α-3 : 4-*Dimethoxy*-6-*ethylphenyl*-β-6-*nitro*-3 : 4-*dimethoxyphenyl acrylic Acid* (VII).—A solution of 5 g. of the previous acid in meth alcohol was neutralised by methyl-alcoholic potassium hydroxid and evaporated in a round-bottom flask. The potassium salt wa dried in a vacuum at 120—130° for 3 hours, and 10 g. of 6-nitr 3 : 4-dimethoxybenzaldehyde (Pschorr, *Ber.*, 1899, **32**, 3412) 8 c.c. of acetic anhydride, and 0·2 g. of anhydrous zinc chlorid were then added. The flask was fitted with a long air-condense and dry nitrogen was very slowly passed over the mixture to preven oxidation. The mixture was heated for 20 hours at 120°, and the for 1 hour on the water-bath after addition of 20 c.c. of water. I was then made alkaline with ammonia and filtered from a brow tar, which was re-extracted with ammonia. After charcoal treat ment, acidification gave a voluminous precipitate of the crude *aci* (yield, 52%), which separated from hot methyl alcohol in yello crystals, m. p. 208° after sintering at 203° (Found : equiv., 41 $C_{21}H_{23}O_8N$ requires equiv., 417).

Amino-acid from the above. The nitro-acid (2·08 g.; 5 millimols was dissolved in 20 c.c. of dilute ammonia, heated to 80°, an slowly added to a reduction mixture at the same temperatur prepared by adding 8 c.c. of 25% ammonia to 9·2 g. of ferrou sulphate (33 millimols.) in a little water. The mixture was shake and left on the water-bath for 2 hours and filtered. Acetic aci precipitated from the dark brown solution a deep yellow, ampho teric precipitate, m. p. 192° in the crude state.

2 : 3 : 5 : 6-*Tetramethoxy*-8-*ethylphenanthrene*-9-*carboxylic Aci* (VIII) *and* 2 : 3 : 5 : 6-*Tetramethoxy*-8-*ethylphenanthrene* (?).—Th above amino-acid (0·9 g.; 2·5 millimols.), dissolved in the calculate quantity of sodium carbonate solution, was mixed with 2·5 c.c. o *N*-sodium nitrite and dropped very slowly into 9 c.c. of well-coole and stirred *N*-sulphuric acid. After filtration, the solution of th diazonium salt was heated for 2 hours on the water-bath; it the no longer coupled with β-naphthol. A reddish-brown acid separate on acidification, but could not be crystallised; yield, 0·5 g. (crude)

A small-scale experiment with amyl nitrite and copper powder in e cold yielded hardly any of the acid after 12 hours. The crude id was decarboxylated by heating 0·2 g. in a bath at 230—250°/ mm. An ethereal solution of the oily distillate, after being ished with sodium carbonate, was evaporated; the residue crystal-ed from hot methyl alcohol in pale brown leaflets, m. p. 106°, d 112° when mixed with the corresponding compound from ırotetanine. The product (some 40 mg.) was redistilled and ystallised as before; it was now completely colourless and melted 118°, but the mixture with the laurotetanine derivative melted 106°. The lowering of the melting point is as yet unexplained; is not clear which of the two substances should first be suspected having a wrong constitution assigned to it. Both substances owed sparing solubility in methyl alcohol.

Some preliminary experiments were also undertaken with lauro-anine ethyl ether, prepared by means of ethyl *p*-toluenesulphonate. ıe oily base gave a hydriodide, m. p. 198—200°, a methiodide, p. 223—226°, a methine methiodide, m. p. 275°, and a trimethoxy-hoxyvinylphenanthrene, m. p. 139°.

6-*Nitro-3-methoxy-4-ethoxybenzaldehyde* (ethyl nitrovanillin) was epared by adding ethyl vanillin to a mixture of equal parts of ming and ordinary concentrated nitric acids. After distillation der reduced pressure, it melted at 159—160° and was resublimed a vacuum at 130—140° (Found: C, 53·3; H, 4·8. $C_{10}H_{11}O_5N$ quires C, 53·3; H, 4·8%). The condensation of this aldehyde th potassium dimethoxyethylphenylacetate has not yet pro-eded in normal fashion.

We wish to express our great indebtedness to Dr. R. Wind, rector of the Experimental Forestry Station, and to Dr. W. octers van Leeuwen, Director of the Botanic Gardens, Buitenzorg, va, for a supply of the bark of *Litsea citrata*; also to Professor . Wright Smith, Director of the Royal Botanic Gardens, Edin-rgh, for help in securing a quantity of *Glaucium luteum*, and to e Moray Fund of Edinburgh University for a grant towards e expenses of the research.

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EDINBURGH UNIVERSITY. [*Received, October 23rd*, 1928.]

CCCLXXXV.—*Some Substitution Products of Azobenzene.*

By JAMES BURNS, HAMILTON McCOMBIE, and HAROLD ARCHIBALD SCARBOROUGH.

AMONG the systems containing two phenyl nuclei which are of interest, from the point of view of substitution, is azobenzene. The order of substitution in this series derives its importance from the fact that the system contains two tervalent nitrogen atoms free from hydrogen atoms; it might be expected, therefore, that analogies in behaviour between this series and nitrosobenzene or the diacyl derivatives of aminodiphenyl (compare Scarborough and Waters, J., 1927, 1139) would be found. The formation of quinonoid compounds in this series is a possibility which must not be excluded as a factor which would influence in a marked manner the sequence in which progressive substitution would occur.

The first substitution reaction in this series was carried out by Laurent and Gerhardt (*Annalen*, 1850, **75**, 73), who examined the reaction between azobenzene and nitric acid. A dibromoazobenzene was obtained by Werigo (*Annalen*, 1865, **135**, 178; 1873, **165**, 199). An extensive study of the substitution products of azobenzene with nitric acid, sulphuric acid, and bromine, in which as many as four similar or dissimilar groups were introduced, was made by Janovsky (*Monatsh.*, 1881, **2**, 221; *et seq.*). The nature of the nitration products of azobenzene which were described by Janovsky was the subject of a mild criticism by Klinger and Zurdeeg (*Annalen*, 1889, **255**, 336); but it remained for Werner and Stiasny (*Ber.*, 1899, **32**, 3257) to point out that of some twelve mono-, di-, and tri-nitro-derivatives of azobenzene, described by Janovsky, there was not one which might be described as a single individual and as a consequence the structures assigned could only be justified in two cases where a reasonable degree of purity had been obtained.

An examination made in these laboratories by Mr. J. Dexter has shown that the destructive criticism of Werner and Stiasny is fully justified; further, he has shown that of the three monobromo- and two dibromo-azobenzenes described by Janovsky, only one mono- and one dibromo-azobenzene could be isolated.

In view of all these criticisms of the work of Janovsky, the remaining substitution products which he obtained cannot be accepted without revision or independent confirmatory evidence.

The number of direct substitution products of azobenzene itself whose constitution may be regarded as established is therefore limited to 4-nitroazobenzene, m. p. 149°, 4 : 4′-dinitroazobenzene,

m. p. 221°, 4-bromoazobenzene, m. p. 94°, 4 : 4′-dibromoazobenzene, m. p. 205°, and azobenzene-4-sulphonic acid, m. p. 127°. It would thus appear that only the two 4-positions are readily substituted.

The introduction of substituents into the molecule of any of the three possible methylazobenzenes (benzeneazotoluenes) does not appear to have been attempted. In an attempt to nitrate 4-methylazobenzene in acetic acid solution the initial substance was recovered, and a nitro-group could only be introduced by the action of fuming nitric acid; whereas 2- and 3-methylazobenzene nitrated easily in acetic acid solution to yield products substituted in the 4 : 4′-positions. On bromination 4-methylazobenzene could only be converted into *4′-bromo-4-methylazobenzene* by the action of neat bromine, whereas 3-methylazobenzene was converted into *4-bromo-3-methylazobenzene* by bromination in acetic acid solution. The product obtained by the action of bromine on 2-methylazobenzene is apparently not an azo-derivative and its constitution could not be elucidated. The nature of the substitution products of 2- and 4-methylazobenzenes indicates that the $C_6H_5{\cdot}N{:}N{\cdot}$ group is more strongly directive than the methyl group; but when in the 2- or 3-position the methyl group makes it possible to effect substitution by less drastic methods than when it occurs in the 4-position and must thus have an activating effect.

The presence of chlorine as a substituent in azobenzene causes further substitution to take place in the unsubstituted phenyl nucleus and, since the $C_6H_5{\cdot}N{:}N{\cdot}$ group is strongly *p*-directive, the entering substituent occupies the 4′-position. Thus on nitration, chlorination and bromination, 4-chloroazobenzene yielded *4′-nitro-*, 4′-chloro-, and *4′-bromo-4-chloroazobenzene*, respectively; similarly, 3-chloroazobenzene yielded *4′-nitro-* and *4′-bromo-3-chloroazobenzene*. This behaviour of the halogen atom was to be expected from a consideration of the results obtained in the diphenyl and benzophenone series.

The further substitution of 4-hydroxyazobenzene was first investigated by Noelting (*Ber.*, 1887, **20**, 2997), who showed that on nitration, in concentrated sulphuric acid solution, 4′-nitro-4-hydroxyazobenzene was formed; it has also been shown by Hewitt (J., 1900, **77**, 99) that if this nitration is carried out in nitric acid (*ca.* 20%) solution the product is 3-nitro-4-hydroxyazobenzene. This difference in behaviour was ascribed to the formation of a salt between the concentrated sulphuric acid and the azophenol, acting in its tautomeric form as quinonephenylhydrazone. In later communications Hewitt and Aston (*ibid.*, pp. 713, 811) have shown that on bromination, in the presence of fused sodium acetate, 4-hydroxyazobenzene yielded a product substituted in the 3 : 5-positions,

whereas bromination in the absence of the sodium acetate yielded 3 : 5 : 4′-tribromo-4-hydroxyazobenzene. It has been found that 4-methoxyazobenzene on chlorination yielded 3 : 5-*dichloro*-4-*methoxyazobenzene*, and regulated bromination gave 3-*bromo*- and 3 : 5 : 4′-*tribromo*-4-*methoxyazobenzenes*. On nitration, 3 : 4′-*dinitro*-4-*methoxyazobenzene* was obtained. It is thus seen that the methoxyl group has a stronger directive effect than the C_6H_5·N:N· group. Since two chlorine atoms enter the methoxylated nucleus successively, and since bromine appears to enter the 4′- and 5-positions simultaneously, it would seem that the C_6H_5·N:N· group, though strongly *p*-directive, tends to lessen the reactivity of the nuclei to which it is attached. This view is supported by the parallel results which were obtained with 4-methoxybenzophenone (Blakey, Jones, and Scarborough, J., 1927, 2865).

The only substitution product of 4-aminoazobenzene or of its acetyl derivative whose structure is established is 4′-nitro-4-acetamidoazobenzene. This compound was formed on nitration in sulphuric acid solution (Friedländer, " Fortschritte in der Teerfarbenfabrikation," IV, 1021).

It has been found that 4-acetamidoazobenzene on chlorination, in acetic acid solution, yielded 3-*chloro*-4-*acetamidoazobenzene*. Attempts to introduce other substituents into the molecule of 4-acetamidoazobenzene failed.

Chlorination of 4-aminoazobenzene in carbon tetrachloride solution yielded an inseparable mixture of di- and tri-chloro-derivatives. In acetic acid solution, the base brominated smoothly and yielded 3 : 5-dibromo-4-aminoazobenzene (compare Berju, *Ber.*, 1884, **17**, 1403). Iodination and nitration were attempted under various conditions, but the product was always a tar.

The difference in structure of the two substitution products of 4-acetamidoazobenzene is the same as that observed in the case of 3-acetamidodiphenyl (Blakey and Scarborough, J., 1927, 3002) and must therefore be ascribed to the influence of a concentrated acid upon the acetamido-group and not to such a change in the structure of the azo-group as occurs in the case of 4-hydroxyazobenzene. The inactive nature of 4-acetamidoazobenzene was an unexpected factor in this section of the work.

For the determination of the structure of the substituted azobenzenes, at least three methods were available :

(*a*) The oxidation of a hydrazo-compound formed by the condensation of appropriately substituted hydrazines and *o*- and *p*-halogenonitrobenzenes.

(*b*) The complete reduction of the compound to its constituent bases, their separation, and identification.

(*c*) The condensation of appropriately substituted nitrosobenzenes and anilines.

Not one of the three methods is free from experimental difficulties, but since the third method leads to the most direct comparison it has been employed in nearly every case. This method, however, proves unsatisfactory or impossible when an *o*-nitro-group or an accumulation of nitro-groups is present in either the nitrosobenzene or the aniline molecule.

EXPERIMENTAL.

4-Methylazobenzene was obtained when a glacial acetic acid solution of equimolecular quantities of nitrosobenzene and *p*-toluidine was kept over-night. It separated from dilute alcohol in deep yellow plates, m. p. 72° (compare Mills, J., 1895, 67, 929).

4′-*Nitro*-4-*methylazobenzene* was prepared by keeping a solution of 5 g. of 4-methylazobenzene in 100 c.c. of nitric acid (*d* 1·5) below 5° for 2 hours. The semi-solid mass which was precipitated when the mixture was poured into water yielded 3·5 g. of pure product. The same substance was obtained by condensing *p*-nitrosotoluene with *p*-nitroaniline. It crystallised from alcohol in deep red needles, m. p. 183° (Found: N, 17·35. $C_{13}H_{11}O_2N_3$ requires N, 17·4%).

4′-*Bromo*-4-*methylazobenzene*.—A solution of 5 g. of 4-methylazobenzene in dry bromine (4 c.c.) was kept for some hours. The residue after removal of the excess of bromine with sodium bisulphite solution was repeatedly crystallised from alcohol and gave orange needles, m. p. 152° (Found: Br, 28·95. $C_{13}H_{11}N_2Br$ requires Br, 29·1%).

3-*Nitro*-4-*methylazobenzene* was obtained when 2-nitro-*p*-toluidine was condensed with nitrosobenzene. It separated from alcohol in long, golden needles, m. p. 105° (Found: N, 17·35. $C_{13}H_{11}O_2N_3$ requires N, 17·4%).

3-*Bromo*-4-*methylazobenzene* was prepared by condensing 2-bromo-*p*-toluidine with nitrosobenzene. It crystallised from alcohol in yellow needles, m. p. 84° (Found: Br, 29·0. $C_{13}H_{11}N_2Br$ requires Br, 29·1%).

ω-*Bromo*-4-*methylazobenzene*.—5 G. of 4-methylazobenzene were dissolved in 80 c.c. of a 10% solution of bromine in acetic acid together with 4 g. of fused sodium acetate and the solution was heated on the water-bath for 8 hours. After some days it deposited about 1 g. of red needles, m. p. 115° after recrystallisation from alcohol (Found: N, 10·25; Br, 29·1. $C_{13}H_{11}N_2Br$ requires N, 10·15; Br, 29·1%). The substance remaining in the acetic acid mother-liquor was unchanged 4-methylazobenzene. The product reacted

with dilute aqueous-alcoholic potash, the bromine being liberate as potassium bromide.

3-Methylazobenzene was prepared by condensing nitrosobenzen with *m*-toluidine. The product was distilled under diminishe pressure and frozen. It is a light red oil, b. p. 165°/15 mm., an solidifies as red needles, m. p. 18°.

4 : 4′-*Dinitro-3-methylazobenzene*.—A solution of 3-methylazo benzene in nitric acid (*d* 1·5) was maintained below 5° for 90 minute The product crystallised from alcohol in bright red needles, m. p 183° (Found : N, 19·75. $C_{13}H_{10}O_4N_4$ requires N, 19·6%).

The compound was completely reduced with stannous chloride i alcoholic hydrochloric acid solution and the mixed bases wer liberated and acetylated in pyridine solution. Diacetyl-*p*-phenylene diamine, m. p. 310°, was isolated from the mixture by crystallisatio from acetone; the acetone mother-liquor was evaporated to drynes and the residue, repeatedly crystallised from glacial acetic acid, gav 2-methyldiacetyl-*p*-phenylenediamine, m. p. 224°.

4-*Bromo-3-methylazobenzene*.—5 G. of 3-methylazobenzene wer dissolved in 40 c.c. of a 10% solution of bromine in acetic acid, and the mixture heated on the water-bath for 6 hours. The produc separated from dilute alcohol in light yellow needles, m. p. 69 (Found : Br, 29·15. $C_{13}H_{11}N_2Br$ requires Br, 29·1%). It wa also obtained when 6-bromo-*m*-toluidine was condensed with nitroso benzene.

2-Methylazobenzene was obtained when nitrosobenzene was con densed with *o*-toluidine. The product, after distillation unde diminished pressure, was a light red oil, b. p. 180°/20 mm.

4 : 4′-*Dinitro-2-methylazobenzene* was prepared by keeping a solu tion of 2-methylazobenzene in nitric acid (*d* 1·5) below 5°. It wa crystallised from alcohol and from acetone, from which it separate in dark red needles, m. p. 220° (Found : N, 19·6. $C_{13}H_{10}O_4N$ requires N, 19·6%).

The compound was completely reduced with stannous chloride i alcoholic hydrochloric acid solution and the liberated bases wer acetylated. Diacetyl-*p*-phenylenediamine, m. p. 310°, and 2 methyldiacetyl-*p*-phenylenediamine, m. p. 224°, were isolated an identified by comparison with synthetic products.

Action of Bromine on 2-Methylazobenzene.—A solution of 5 g. o 2-methylazobenzene in 120 c.c. of a 10% solution of bromine i glacial acetic acid containing 5 g. of fused sodium acetate, afte standing at room temperature for some hours, deposited whit needles (4 g.), m. p. 210° after recrystallisation from much aceton (Found : C, 35·0, 35·4; H, 1·75, 1·65; N, 6·6, 6·4; Br, 57·5, 57·3 *M*, in bromoform, 390, 403. $C_{13}H_9N_2Br_3$ requires C, 36·0; H, 2·1

N, 6·5; Br, 55·4%; *M*, 433). This *substance* appeared to be unattacked by aqueous permanganate or by stannous chloride in alcoholic hydrochloric acid solution.

4-Chloroazobenzene was obtained when *p*-chloroaniline was condensed with nitrosobenzene. It separated from alcohol in red plates, m. p. 92°.

4-*Chloro*-4′-*bromoazobenzene*.—5 G. of 4-chloroazobenzene were intimately mixed with 0·5 g. of ferric chloride, and 4 g. of bromine added; after the reaction had become less violent, 10 c.c. of water were added and the paste was heated on the water-bath for 1 hour. The product crystallised from acetone in bright yellow needles, m. p. 195° (Found: 0·1859 g. gave 0·2097 g. of silver halides. Theory requires 0·2095 g.).

The same product was obtained when *p*-chloronitrosobenzene was condensed with *p*-bromoaniline.

4 : 4′-*Dichloroazobenzene*.—5 G. of 4-chloroazobenzene were intimately mixed with 0·5 g. of ferric chloride and chlorine in excess was passed into the molten mass at water-bath temperature. After the mass had solidified, it crystallised from acetone in light yellow needles, m. p. 188° (Found: Cl, 28·4. Calc. for $C_{12}H_8N_2Cl_2$: Cl, 28·3%). Busch and Hobein (*Ber.*, 1907, **40**, 2099) give m. p. 184°.

p-Chloronitrosobenzene was condensed with *p*-chloroaniline in acetic acid solution and the same product was obtained.

4 : 4′-*Dichloroazoxybenzene*.—5 G. of 4 : 4′-dichloroazobenzene, dissolved in acetic acid, were treated with 8 g. of "Hyperol," added in small portions; the temperature was that of the water-bath. The product separated on standing over-night and crystallised from alcohol in light straw-coloured needles, m. p. 157° (Found: Cl, 26·7. $C_{12}H_8ON_2Cl_2$ requires Cl, 26·6%).

4-*Chloro*-4′-*nitroazobenzene* was prepared by dissolving 4-chloroazobenzene in nitric acid (*d* 1·5) and keeping this solution below 10° for 30 minutes. It separated from alcohol in long red needles, m. p. 169° (Found: Cl, 13·45. $C_{12}H_8O_2N_3Cl$ requires Cl, 13·55%).

The same compound was obtained when *p*-nitroaniline was condensed with *p*-chloronitrosobenzene, in acetic acid solution, at the temperature of the water-bath.

3-Chloroazobenzene was prepared by the condensation of nitrosobenzene with *m*-chloroaniline. It separated from alcohol in orange-red needles, m. p. 68° (compare Bamberger, *Ber.*, 1896, **29**, 103).

3-*Chloro*-4′-*nitroazobenzene*.—5 G. of 3-chloroazobenzene were dissolved in 80 c.c. of nitric acid (*d* 1·16) and the temperature was maintained at 0° for 20 minutes. The product separated from alcohol in red needles, m. p. 129° (Found: N, 16·15. $C_{12}H_8O_2N_3Cl$ requires

The same compound was obtained when *m*-chloronitrosobenzene was condensed with *p*-nitroaniline.

3-Chloro-4′-bromoazobenzene.—5 G. of 3-chloroazobenzene were ground into a paste with 5 c.c. of a concentrated ferric chloride solution, 5 c.c. of bromine were added, and the mixture was heated on the water-bath for 30 minutes. After repeated crystallisations from alcohol the product separated in deep yellow needles, m. p. 128° (Found : 0·1736 g. gave 0·1947 g. of silver halides. Theory requires 0·1950 g.). The same product was obtained when *m*-chloronitrosobenzene was condensed with *p*-bromoaniline.

4-Methoxyazobenzene was prepared by condensing nitrosobenzene with *p*-anisidine. It separated from alcohol in bright yellow plates, m. p. 64°.

3-Bromo-4-methoxyazobenzene.—5 G. of 4-methoxyazobenzene, 4 g. of fused sodium acetate, and 7·5 g. of bromine in 100 c.c. of acetic acid were heated on the water-bath for 4 hours. The product separated from alcohol in long yellow needles, m. p. 78° (Found : Br, 27·65. $C_{13}H_{11}ON_2Br$ requires Br, 27·5%).

2-Bromo-4-nitroanisole was prepared by adding bromine (1 mol.) to 4-nitroanisole in the presence of a little pyridine; the product separated from dilute alcohol in long needles, m. p. 108° (Found : Br, 34·6. $C_7H_6O_3NBr$ requires Br, 34·5%). The corresponding base, *obtained by reduction with stannous chloride in alcoholic* hydrochloric acid solution, was condensed with nitrosobenzene, and 3-bromo-4-methoxyazobenzene resulted.

3 : 4′-*Dibromo-4-methoxyazobenzene* was obtained when *p*-bromonitrosobenzene was condensed with 2-bromo-4-anisidine. It separated from alcohol in light yellow needles, m. p. 123° (Found : Br, 43·25. $C_{13}H_{10}ON_2Br_2$ requires Br, 43·3%).

3 : 4′ : 5-*Tribromo-4-methoxyazobenzene.*—(*a*) A solution of 5 g. of 4-methoxyazobenzene and 10 g. of fused sodium acetate in 100 c.c. of a 30% solution of bromine in acetic acid was heated on the water-bath for 24 hours and finally refluxed for about 30 minutes. Crystals separated on cooling. (*b*) 3-Bromo- and 3 : 4′-dibromo-4-methoxyazobenzenes were treated in the same manner. The *compound* crystallised from much alcohol in yellow needles, m. p. 130° (Found : Br, 53·6. $C_{13}H_9ON_2Br_3$ requires Br, 53·5%).

3 : 5-*Dichloro-4-methoxyazobenzene* was prepared by passing dry chlorine into a mixture of 5 g. of 4-methoxyazobenzene and 5 g. of sodium acetate in 100 c.c. of acetic acid until the solution was saturated. It crystallised from alcohol in long yellow needles, m. p. 98° (Found : Cl, 25·35. $C_{13}H_{10}ON_2Cl_2$ requires Cl, 25·3%).

3 : 5-*Dichloro-4-hydroxyazobenzene* was obtained when (*a*) 3 : 5-dichloro-4-methoxyazobenzene was refluxed with a mixture of

constant-boiling hydrobromic acid and acetic acid for 8 hours; and (*b*) nitrosobenzene was condensed with 2 : 6-dichloro-4-aminophenol in acetic acid solution. It separated from alcohol in brownish needles, m. p. 116° (Found: Cl, 26·5. $C_{12}H_8ON_2Cl_2$ requires Cl, 26·6%).

3 : 4'-*Dinitro-4-methoxyazobenzene*.—A solution of 5 g. of 4-methoxyazobenzene in 30 c.c. of sulphuric acid was treated with 5 g. of potassium nitrate and kept for 24 hours. The product separated from acetone in bright red needles, m. p. 190° (Found: N, 18·6. $C_{13}H_{10}O_5N_4$ requires N, 18·55%). The compound was completely reduced with stannous chloride in alcoholic hydrochloric acid solution and the bases were liberated and acetylated in pyridine solution. Diacetyl-*p*-phenylenediamine, m. p. 310°, was isolated.

4-*Aminoazobenzene was prepared according to Staedel and Bauer* (*Ber.*, 1886, **19**, 1953) and converted into 4-acetamidoazobenzene with acetic anhydride; this separated from dilute alcohol in needles, m. p. 144°.

3-*Chloro-4-acetamidoazobenzene*.—A 5% solution of 4-acetamidoazobenzene in glacial acetic acid together with an excess of fused sodium acetate was treated with dry chlorine at 10° until the solution was saturated. The product crystallised from alcohol in orange plates, m. p. 134° (Found: Cl, 13·0. $C_{14}H_{12}ON_3Cl$ requires Cl, 13·0%).

3-*Chloro-4-aminoazobenzene* was obtained when the acetyl derivative was refluxed with alcoholic hydrochloric acid for 6 hours. The base, which was liberated with dilute ammonia, crystallised from dilute alcohol in deep yellow needles, m. p. 99·5° (Found: Cl, 15·2. $C_{12}H_{10}N_3Cl$ requires Cl, 15·3%). The compound was diazotised in alcoholic solution and, after refluxing, 3-chloroazobenzene, m. p. 67·5°, was isolated.

2-*Chlorobenzidine* was obtained when 3-chloroazobenzene was refluxed with stannous chloride in alcoholic hydrochloric acid solution for 2 hours. It separated from dilute alcohol in long needles, m. p. 113° (Found: Cl, 16·3. $C_{12}H_{11}N_2Cl$ requires Cl, 16·2%).

3 : 5-*Dibromo-4-aminoazobenzene*.—10 G. of 4-aminoazobenzene, dissolved in 100 c.c. of acetic acid, together with 10 g. of fused sodium acetate, were treated with 180 c.c. of a 10% solution of bromine in acetic acid at 15°. The base crystallised from much alcohol in light yellow needles, m. p. 168° (compare Hewitt, *Ber.*, 1908, 41, 1986) (Found: Br, 44·9. Calc. for $C_{12}H_9N_3Br_2$: Br, 45·05%). On reduction with stannous chloride in alcoholic hydrochloric acid solution a mixture of aniline and 2 -dibromo-*p*-phenylenediamine was obtained. The latter base crystallised from water in long silky needles, m. p. 136° (Found: Br, 60·15. Calc. for $C_6H_6N_2Br_2$:

Br, 60·15%). Hewitt and Walker (J., 1907, **91**, 1141) give m. p 137°.

3 : 5-*Dibromoazobenzene* was obtained when (*a*) 3 : 5-dibromo-4 aminoazobenzene was diazotised with amyl nitrite in alcoholic solution; or (*b*) nitrosobenzene was condensed with 3 : 5-dibromo aniline. It separated from alcohol in dark red needles, m. p. 104° (Found: Br, 46·9. $C_{12}H_8N_2Br_2$ requires Br, 47·0%). On bromin ation in acetic acid solution at water-bath temperature, this com pound gave 2 : 4 : 6-tribromoaniline, m. p. 119°.

3 : 5-*Dibromohydrazobenzene*.—5 G. of 3 : 5-dibromoazobenzene in 250 c.c. of alcohol were refluxed for 2 hours with 8·5 g. of stannous chloride and 10 g. of sodium hydroxide, also dissolved in 250 c.c. of alcohol. The alcohol was partly removed, the residue poured into water, and the product extracted with ether. It separated from light petroleum (b. p. 60—70°) in small plates, m. p. 114° (Found Br, 46·7. $C_{12}H_{10}N_2Br_2$ requires Br, 46·75%).

2 : 6-*Dibromobenzidine* was obtained when (*a*) 3 : 5-dibromoazo benzene was reduced with stannous chloride in alcoholic hydrochloric acid solution; and (*b*) 3 : 5-dibromohydrazobenzene was refluxed with an excess of concentrated hydrochloric acid for 30 minutes It crystallised from dilute alcohol in needles, m. p. 185° (Found Br, 46·8. $C_{12}H_{10}N_2Br_2$ requires Br, 46·75%).

One of the authors (J. B.) wishes to express his thanks to the Executive Committee of the Carnegie Trust for a Research Fellow ship which has enabled him to collaborate in this work.

THE UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, August 22nd*, 1928.]

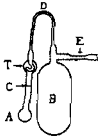
CCCLXXXVI.—*Determination of the Pressure and Density of Moist, Saturated Ammonium Bromide Vapour.*

By ANDREAS SMITS and RONALD PURCELL.

THIS investigation originated in the intention to apply the densi tensimeter (this vol., p. 2409) to a study of the influence of intensive drying on the vapour pressure and density of ammonium bromide The moist material was first reinvestigated in this apparatus, which enables the pressure and density to be determined simultaneously and thus avoids a source of error occurring in experiments where the pressure is measured first and the density subsequently in a separate apparatus. For example, the method used by Smith and Lombard

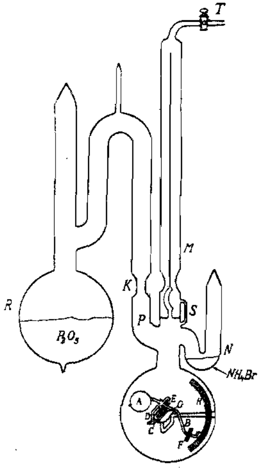
(*J. Amer. Chem. Soc.*, 1915, **37**, 38) is open to criticism unless it is certain that the large bulb, B (Fig. 1), was never at a lower temperature than the small one, A, while the apparatus was attaining the temperature of the bath; but since, in order to hold the apparatus firmly in the bath, the bulb was wired to an iron rod protected with asbestos paper, it is probable that when the capillary, D, was sealed some solid as well as vapour was in the bulb B. Any adsorption of vapour on the walls will introduce an error in the same direction, *i.e.*, giving too high a vapour density.

FIG. 1.



With the densi-tensimeter, it is possible to prevent solid being deposited on the surface of the baroscope by taking readings after the apparatus is cooled from a higher to a lower temperature. During the cooling, the silica baroscope is a little warmer than the outer glass wall of the flask, and consequently all salt sublimes on to the latter. Moreover, the newest baroscopes are so constructed that the error caused by adsorption is negligible.

FIG. 2.



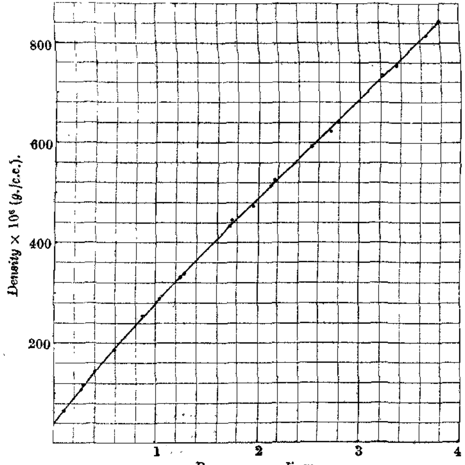
EXPERIMENTAL.

Fig. 2 shows the bulb containing the baroscope sealed to the glass-spring indicator. The figure also shows, however, a bulb with phosphoric oxide, which was not present in these experiments with the moist substance—in this case tube P was sealed off at K. This apparatus was cleaned with boiling nitric–chromic acid mixture, washed, steamed, and dried. The baroscope was then calibrated at 100°, 306°, and 394° by altering the pressure of the air in the instrument and reading the position of the pointer of the baroscope. The density (g./c.c.) of the air was then calculated and plotted against the baroscope readings, thus giving a calibration curve (see Table I and Fig. 3).

TABLE I.

Temp. 100°. Baroscope reading.	$d \times 10^6$.	306°. Baroscope reading.	$d \times 10^6$.	394°. Baroscope reading.	$d \times 10^6$.
3·80	845	3·72	820	3·68	819
3·22	737	2·71	624	3·36	756
2·52	596	1·95	476	2·78	642
2·16	527	1·28	336	2·13	517
1·75	447	1·04	288	1·72	439
1·25	330	0·60	184	1·42	372
1·01	280	0·40	142	0·88	257
0·27	108	0·10	61	0·28	114

FIG. 3.



After calibration, the apparatus was heated to near the softenin point of the glass in a stream of dry oxygen. The ammoniu bromide was introduced into the bend of the tube N (Fig. 2), whic was then resealed, and the apparatus connected to the high-vacuu pump through tap T. After exhaustion, this tap was closed, and th thin tube, S (called the bridge), sealed off. The apparatus wa placed vertically, and the zero position of the glass-spring indicat ascerta

The apparatus was then placed in a bath of fused potassium and odium nitrates contained in a 4-litre Pyrex-glass beaker. With uitable illumination, the position of the needle of the baroscope ould be read with the aid of a small telescope. The beaker was laced over a large double-ring gas burner and surrounded by an sbestos hood, in which two holes were made to permit baroscope eadings to be taken. Two large Bunsen burners, for regulation f the temperature, also passed through this hood.

The top of the hood was covered with asbestos board, through hich passed the mantle of the densi-tensimeter, a resistance hermometer, and a stirrer. It was possible to detect a change of ·005° with the thermometer, and the bath could be readily kept onstant to within 0·1° during a reading by means of a specially esigned stirrer with ball bearings, which was driven at 800 r.p.m. number of simultaneous readings of the vapour pressure (p in m. Hg) and baroscope positions were then made at temperatures etween 330° and 400°. The results of these are given in Table II. he densities, d, were read from the calibration curve, and the apour densities, $D (= \frac{1}{2}M)$, calculated from this, on the assumption hat the gas laws were obeyed :

$$D = 22{\cdot}4 \times d \times T \times 760/(2 \times 273 \times p).$$

TABLE II.

Results with damp ammonium bromide.

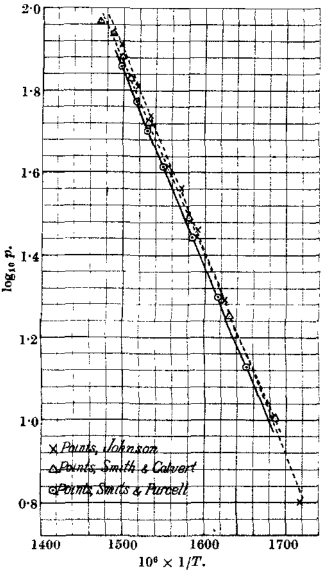
No.	Temp.	$10^6 \times 1/T$.	p.	$\text{Log}_{10}\, p$.	Baroscope readings.	$d \times 10^6$.	D.
1	331·8°	1651	13·4	1·1271			
2	345·6	1617	19·9	1·2987	0·88	250	24·2
4	357·7	1585	27·8	1·4442	1·29	340	24·0
5	364·3	1569	33·1	1·5195	1·52	394	23·7
6	372·1	1550	41·1	1·6137	1·91(?)	474	23·2(?)
7	380·7	1530	50·5	1·7021	2·52	590	23·8
8	386·7	1516	59·7	1·7759	2·95	660	23·4
9	395·0	1497	72·7	1·8613	3·67	820	23·5
						Average	23·7

When log p is plotted against $1/T$ (the reciprocal of the absolute emperature), the points on Fig. 4 are obtained. It will be seen hat they lie on a straight line, thus showing that the heat of vaporation is not a function of temperature within the range vestigated. This result is in agreement with the values of the ensities in the last column, which correspond closely with complete issociation, the calculated value being 24·5. It will be noticed, owever, that the values found are even lower than this. An error n this direction will be introduced if there is any adsorption on the ulb of the baroscope, and, as shown later, there is sufficient adsorp-

tion to give such an error, but when this is eliminated, the resul corresponds exactly with complete dissociation.

The above results are represented graphically in Fig. 5, where th vapour pressures are plotted against the temperature, the determin ations by Smith and Calvert (*J. Amer. Chem. Soc.*, 1914, **36**, 1368 and by Johnson (*Z physikal. Chem.*, 190ξ **56**, 39) being inserte for reference. It wil be noted that ou values are slightl below those of th earlier workers. Th vapour densities hav been determined b Deville and Troost an by Smith and Lom bard (*loc. cit.*). Th former found complet dissociation at 440 and 860°, whilst th latter found a *chang from* 48% *dissociatio at* 300° *to* 10% *at* 390 The measurements c Smith and his cc workers would seem t be beyond criticisn but closer conside ation shows that a error must have bee introduced, for whe the logarithms of the vapour pressures a plotted against $1/T$ straight line is ob tained (see Fig. 4). This indicates that the heat of evaporation i *not* a temperature function, and hence that the degree of dissociatio cannot change appreciably unless the heat of dissociation is ver small; but since this is known not to be the case, most probably th dissociation is complete. Hence it was thought that Smith an Lombard's density determinations were incorrect, and an independe method of checking the results was sought.

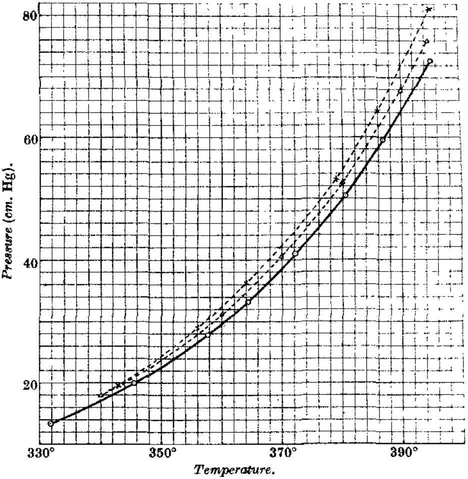
FIG. 4.



We therefore determined the vapour density in yet anoth

way, namely, by what we called the "extrapolation method." A vapour-pressure apparatus of known volume was filled with a known weight of ammonium bromide, highly evacuated, and the bridge sealed off. The vapour density could be determined by measuring first the pressure curve of the saturated vapour and then the Boyle–Gay-Lussac line or the curve of the unsaturated vapour, since, from the point of intersection of the lines obtained by plotting

FIG. 5.



× *Johnson.* △ *Smith and Calvert.* ⊙ *Smits and Purcell.*

log p against $1/T$, the vapour density of the just-saturated vapour is readily calculated. Table III gives the results obtained with a glass apparatus and two other experiments with glass and quartz apparatus gave similar results. These three experiments carried out in this manner, with an apparatus of Durobax glass and quartz, gave the results in Table IV, in which the pressure and temperature refer to the points of intersection. These points had to be found by extending the two lines mentioned above, since experimentally we

TABLE III.

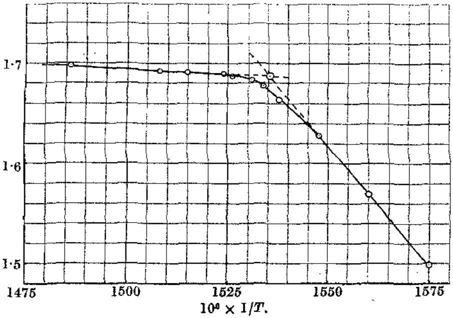
Vapour pressures and temperatures (Expt. 1; glass apparatus).

Temp.	p.	$10^6/T$.	$\text{Log}_{10}\,p$.	Temp.	p.	$10^6/T$.	$\text{Log}_{10}\,p$.
362·0°	31·5	1575	1·4983	381·5°	48·7	1526	1·6875
367·8	37·1	1560	1·5691	383·2	49·0	1524	1·6902
373·2	42·4	1548	1·6274	387·0	49·1	1515	1·6911
376·7	46·1	1538	1·6637	390·4	49·3	1508	1·6928
378·9	47·5	1534	1·6767	399·6	49·9	1486	1·6981
379·9	48·3	1531	1·6839				

TABLE IV.

Apparatus.	Glass, I.	Glass, II.	Quartz, III.
Weight of NH_4Br, g.	0·3404	0·2108	0·1376
Volume of bulb, c.c.	580·3	303·9	310·0
Temp.	379·0°	385·0°	369·0°
Pressure, p	48·7	58·0	36·5
D	24·6	24·5	24·4

FIG. 6.



Intersection point: $\log p = 1·6875$. $p = 48·7$ *cm.* Hg. $1/T = 0·001535$. $t = 379°$.

did not find an intersection but a continuous change of one line into the other (see Fig. 6).

This remarkable fact proves that there is a perceptible adsorption caused by the glass wall. So long as there is an excess of solid substance, this adsorption does not exert any influence on the vapour pressure, but when the solid substance has apparently just disappeared there is still a small quantity adsorbed by the wall of the vessel, which is gradually liberated at higher temperatures. The effect is that with rising temperature the curve of the saturated vapour pressures is left at too low a temperature and the Boyle–Gay-Lussac

ne is reached at too high a temperature. Between these two the ressure is abnormally low. Both glass and quartz behaved in the ame way. This phenomenon, which has also been found with ercuric iodide (Rinse, this vol., p. 1442), interested us, since it xplained the slightly low values of vapour densities determined ith our baroscope. The adsorption per sq. cm. of silica surface of he apparatus can be calculated, and from this result we find that he weight of adsorbed material on the baroscope is just sufficient o account for the low values. Though the differences are rather mall, Smits thought it advisable to change the construction of the aroscope once more, in order to eliminate the error, and this was ffected by having equal silica surfaces on each side (this vol., p. 2410).

Finally, the value of the heat of evaporation can be calculated from ur results. From the formula, $d \log_e p/dT = Q/RT^2$, it follows that $\log_e p/d\left(\frac{1}{T}\right) = Q/R$. Now it has been shown that $\log_{10} p$ is a near function of $1/T$, which proves that Q is not a temperature unction. In agreement with this, the vapour-density determintions showed that the dissociation of ammonium bromide in the apour state from 330—400° is complete. Consequently we can rite $2{\cdot}303 \log_{10} p = -Q/RT + C$. From Fig. 4, using Briggsian ogarithms, we read,

or $1/T_1 = 0{\cdot}001651, \log_{10} p_1 = 1{\cdot}1271,$

nd for $1/T_2 = 0{\cdot}001497, \log_{10} p_2 = 1{\cdot}8613,$

ence $$Q/R = \frac{2{\cdot}303(1{\cdot}8613 - 1{\cdot}1271)}{1651 \times 10^{-6} - 1497 \times 10^{-6}} = 10980$$

r $Q = 22 \times 10^3$ cals. This value refers to 1 g.-mol. of vapour, and ince the salt is completely dissociated, it corresponds to 1/2 g.-mol. f ammonium bromide; thus $(Q_{SG})_{NH_4Br} = 44 \times 10^3$ cals. The value iven by Johnson, *viz.*, $45{\cdot}4 \times 10^3$ cals., differs somewhat from this.

The value of C follows from

$$C = \frac{2{\cdot}303(T_2 \log p_2 - T_1 \log p_1)}{T_2 - T_1} = 20{\cdot}8$$

o that $\log_e p = -\frac{10980}{T} + 20{\cdot}8.$

Summary.

Using a new apparatus, the " densi-tensimeter " (see Smits, this ol., p. 2409), we have measured simultaneously the vapour pressures nd vapour densities of ammonium bromide. When log p was lotted against $1/T$, a straight line was obtained, from which it ollows that the latent heat of evaporation between 300° and 400° is

not a function of temperature. This result indicated that most probably the vapour would be completely dissociated, and the density determinations with the baroscope showed, in fact, a total dissociation.

The cause of the discrepancy between this result and that of Smith and his co-workers is discussed, and a possible source of error in their work is indicated.

In order to check the density determinations, the authors applied the "extrapolation method," measuring the pressure of the saturated and of the unsaturated vapour of a weighed quantity of salt in a known volume. The plot of log p against $1/T$ gave two straight lines, and when these were produced, their point of intersection gave the pressure and temperature of the just-saturated vapour, from which it was calculated that the corresponding vapour density agreed with complete dissociation.

The two straight lines did not actually intersect, however, but curved and merged into one another, thus indicating a perceptible adsorption on the wall of the apparatus.

Calculation indicated that if the baroscope reading was corrected for this adsorption the result agreed with that obtained by the second method.

The heat of evaporation of ammonium bromide was calculated from the experimental data and found to be 44,000 cals.

THE UNIVERSITY, AMSTERDAM. [*Received, July 13th, 1928.*]

CCCLXXXVII.—*Determination of the Pressure and Density of Moist, Saturated Ammonium Chloride Vapour.*

By ANDREAS SMITS and WILHELMUS DE LANGE.

IN the course of our study of the influence of intensive drying on the pressure and density of saturated ammonium chloride vapour by means of the densi-tensimeter (this vol., p. 2409), we required, as in the case of ammonium bromide (Smits and Purcell, preceding paper), accurate data for the moist material, and as Braune and Knoke (*Z. physikal. Chem.*, 1928, **135**, 49) have recently described experiments on this subject, we thought it desirable to publish this part of our study at once.

For the solution of the "ammonium chloride problem," it was necessary to determine the vapour pressure of the solid and the density of the saturated vapour simultaneously, and this is rendered possible by our densi-tensimeter. In previous determinations of

the density of the saturated vapour, the vapour pressure of the solid was measured first, and the density was subsequently found either by sealing off a bulb of the same apparatus (Johnson, *ibid.*, 1908, **61**, 457), or by use of a separate apparatus, care being taken that the apparatus was filled with the saturated vapour (Smith and Lombard, *J. Amer. Chem. Soc.*, 1915, **37**, 38). As already explained (Smits and Purcell, *loc. cit.*), however, the possibilities of error in such determinations are considerable, for the density bulb which must be sealed off may never have been at a lower temperature than the bulb with the solid ammonium chloride. Johnson intentionally kept the density bulb at a slightly higher temperature than the solid snbstance. On the other hand, Smith and Lombard wished to determine the density of the completely satnrated vapour, and therefore tried to keep the bulb containing solid ammonium chloride and the density bulb at exactly the same temperature; Smits and Purcell, however, adduced a reason why these authors did not succeed in the case of ammonium bromide, and it is now shown that their results for ammonium chloride also are incorrect, probably for a similar reason. Braune and Knoke tried to avoid the difficulty. They first determined the pressure of the saturated vapour in an apparatus of known volume, and after the solid substance had disappeared and the vapour had become unsaturated, they continued the pressure reading at different temperatnres. Then all the salt was condensed in a bulb which was sealed off, and the quantity of salt was thus determined. They therefore found the density of almost saturated and of less saturated vapour.*

Our purpose was to find the density of the completely *saturated* vapour by the two different methods described by Smits and Purcell (*loc. cit.*).

In the second method (the "extrapolation method"), it was shown that any error introduced by adsorption of vapour on the wall of the density bulb could be detected and an appropriate correction made in the density.

Experiments with the Densi-tensimeter.

We used two baroscopes, A and B, which correspond respectively to Figs. 2 and 3 given in the description of this apparatus (this vol., p. 2409), and the method by which they are sealed to the

* Braune and Knoke did not use the glass-spring indicator, the zero position of which, as we stated long ago, is independent of temperature, but they used a glass spiral, of which the position is influenced by temperature, so they were obliged to apply a correction.

The vapour pressures indicated in their tables as "*Dissoziations-drucke*" are much too low.

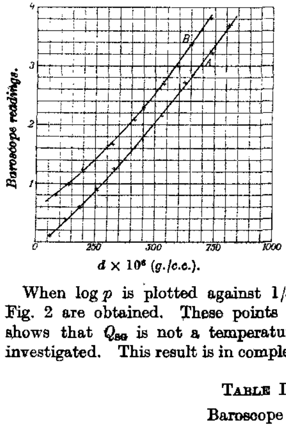
vapour-pressure apparatus with the glass-spring indicator is shown in the paper of Smits and Purcell (Fig. 2), where details of the method of using the apparatus are also to be found.

The two baroscopes were calibrated at different temperatures as already described. The data for baroscope A are those already given; those for B are in Table I, and the two calibration curves are shown in Fig. 1. The vapour densities are calculated from the densities (d; in g./c.c.) read from the calibration curves by the formula :

$$D = \tfrac{1}{2}M = 224 \times 76dT/2 \times 273p = 31{\cdot}18dT/p.$$

After the necessary preliminary operations, a number of simultaneous readings were made at temperatures between 254° and 353°. The densities were read from the calibration curve and the vapour densities calculated. A few of the results are shown in Table II, where p is given in cm. of mercury; the other points are included in Figs. 2 and 3. Both baroscopes give identical results, and since the theoretical value for complete dissociation is $\tfrac{1}{4} \times 53{\cdot}5 = 13{\cdot}4$, it follows that the saturated vapour in the temperature range 280—340° is completely dissociated.

FIG. 1.



When $\log p$ is plotted against $1/T$, the points marked ⊙ in Fig. 2 are obtained. These points lie on a straight line, which shows that Q_{sa} is not a temperature function within the range investigated. This result is in complete agreement with the density

TABLE I.

Baroscope B.

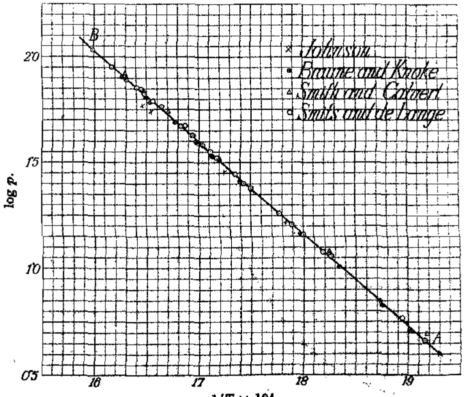
Temp. 100°.		265°.		311°.	
Baroscope reading.	$d \times 10^6$.	Baroscope reading.	$d \times 10^6$.	Baroscope reading.	$d \times 10^6$.
[illegible]72	702	3·81	732	3·36	651
[illegible]95	581	3·00	597	3·11	608
[illegible]70	533	2·59	520	2·61	524
[illegible]	415	1·78	335	2·28	450
[illegible]	335	1·23	196	1·67	321
[illegible]	135	1·01	130	1·14	178
[illegible]	116	0·91	113	0·80	83

TABLE II.

Vapour densities of damp ammonium chloride.

Temp.	T.	$10^6/T$.	p.	$\log_{10} p$.	Baroscope reading.	$d \times 10^6$.	D.
			Baroscope A.				
254·9°	527·9	1894	5·87	0·769	—	—	—
303·4	576·4	1735	27·95	1·446	—	—	—
311·5	584·5	1711	35·84	1·554	0·91	269	13·6
320·2	593·2	1686	47·10	1·673	1·29	347	13·5
328·5	601·5	1663	58·00	1·763	1·62	414	13·3
335·4	608·4	1644	70·18	1·846	2·04	500	13·4
341·0	614·0	1629	80·43	1·905	2·38	570	13·5
352·6	625·6	1598	108·13	2·034	—	—	—
			Baroscope B.				
277·0	550·0	1818	12·02	1·080	—	—	—
282·4	555·4	1800	14·58	1·164	0·94	116	13·7
289·8	562·8	1777	18·22	1·261	1·02	141	13·5
300·7	573·7	1743	25·29	1·403	1·19	189	13·3
314·1	587·1	1703	38·16	1·582	1·55	284	13·5
346·0	619·0	1616	89·25	1·951	—	—	—
						Mean	13·48

FIG. 2.

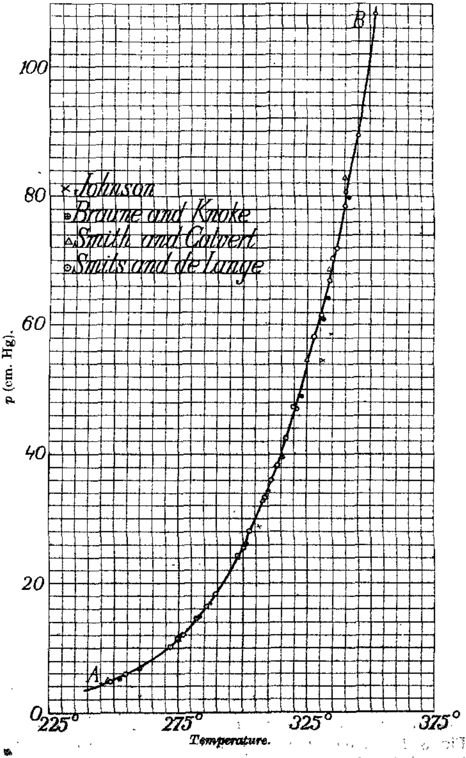


leterminations, corresponding with practically total dissociation. In Fig. 3 the vapour pressure is plotted against the temperature, gain marked ⊙.

The extrapolation method for the determination of the vapour

density was then used in order to find whether adsorption occurred, and if so, to what extent. A vapour-pressure apparatus of known

Fig. 3.



volume was therefore filled with a known weight of ammonium chloride, highly evacuated, and the bridge sealed off. The pressure

›f the saturated vapour was measured first and then the Boyle–Gay-Lussac line, or the curve of the unsaturated vapour. The point of intersection of the lines obtained by plotting log p against $/T$ enables the vapour density of the just-saturated vapour to be calculated.

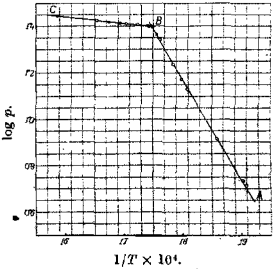
Two series of experiments were carried out with a quartz-appar-.tus with both rising and falling temperatures, and readings were ecorded only after the vapour pressure at any one temperature had een constant for an hour. The results are in Table III.

TABLE III.

Temp.	T.	$10^6/T$.	p.	$\log_{10}p$.	Temp.	T.	$10^6/T$.	p.	$\log_{10}p$.
251·0°	524·0	1909	5·20	0·716	280·2°	553·2	1808	13·51	1·131
264·9	537·9	1859	8·26	0·917	300·6	573·6	1743	24·96	1·397
317·5	590·5	1693	25·96	1·414	314·3	587·3	1703	25·72	1·410
331·9	604·9	1653	26·68	1·426	300·5	573·5	1745	25·14	1·400
357·4	630·4	1586	27·89	1·445	294·6	267·6	1762	21·95	1·341
324·8	597·8	1673	26·22	1·419	287·6	560·6	1784	17·81	1·236
307·5	380·5	1723	25·57	1·408	296·6	569·6	1755	23·10	1·364
					301·5	574·5	1741	25·18	1·401
					283·2	556·2	1798	14·87	1·172
					252·3	525·3	1904	5·46	0·787

When log p is plotted against $1/T$, two straight lines (Fig. 4) are ›btained; these intersect in a point such that log $p = 1{\cdot}399$ and $/T = 0{\cdot}001746$, *i.e.*, $p = 25{\cdot}06$ m. and $T = 572{\cdot}7$. Since he volume of the apparatus vas 314·7 c.c. and the weight ›f ammonium chloride 59·6 ng., the density is *13·4*, which s just the theoretical value or complete dissociation, vhereas the densi-tensimeter ;ave *13·48*.

FIG. 4.

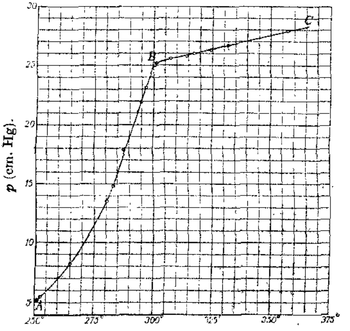


$1/T \times 10^4$.

These determinations were .lso important in deciding vhether there was any per-ceptible adsorption by the ;uartz wall, as in the case of .mmonium bromide. From Fig. 4, and also from Fig. 5, in which p is plotted against temper-ture, it is seen that if a continuous change of one line into the other xists at all it can only occur over an exceedingly small range of emperature, and hence, unlike the bromide, ammonium chloride s not perceptibly adsorbed by the quartz wall, and the same remarks pply to glass. This explains why both forms of the baroscope

The points derived from other workers' determinations of the vapour pressure have been inserted in Figs. 2 and 3. It will be noted that the values of Johnson are not very correct; those of Smith and Calvert (*J. Amer. Chem. Soc.*, 1914, **36**, 1363) and of Braune and Knoke are much better. If Smith and Calvert had plotted a curve as in Fig. 2, they would have found that their points lie on a straight line, and hence that the heat of evaporation is not a temperature function and the degree of dissociation could not change appreciably, unless the heat of dissociation were very small, which is known not to be the case. Consequently, before we

FIG. 5.



started our vapour-density determinations it was already almost certain that practically complete dissociation would be found. Smith and Lombard (*loc. cit.*), however, found a dissociation varying from 55·5 to 63·6% in the temperature range 280—333°.

Earlier workers, *viz.*, Deville and Troost (*Ann. Chim. Phys.*, 1860, **58**, 257; *Compt. rend.*, 1859, **49**, 242), Ramsay and Young (*Phil. Trans.*, 1886, **177**, 99), and Pullinger and Gardner (P., 1891, **7**, 2), applying respectively the methods of Dumas, Hofmann, and Victor Meyer, found degrees of dissociation of 82—98% between 280° and 400°, but Smith thought that the difference between these values and his own was due to the fact that most of the earlier determinations related to unsaturated vapour and that, in consequence of the slow evaporation, the Victor Meyer method did not give exact results, owing to diffusion before the reading could be taken,

Similarly, Smith contended that other high degrees of dissociation (*e.g.* 100% and 91% at 350°, Baker, J., 1894, **65**, 611; 95% at 380°, Gutmann, *Annalen*, 1898, **299**, 282; 98% at 322°, Johnson, *loc. cit.*) were due to the vapour being unsaturated in these cases also. Our determinations, carried out in two different ways, prove, however, that Smith and Lombard's density determinations must have been incorrect for reasons already given (Smits and Purcell, *loc. cit.*), and the measurements of Braune and Knoke, relating to vapours some of which were almost saturated, also indicated complete dissociation.*

Finally, the heat of evaporation and the constant C in the vapour-pressure formula $2{\cdot}303 \log_{10} p = -Q/RT + C$ can be calculated from our results by applying the methods used by Smits and Purcell (*loc. cit.*). From our graph we have

for $\quad 1/T_1 = 0{\cdot}001900, \log p_1 = 0{\cdot}735,$

and for $\quad 1/T_2 = 0{\cdot}001600, \log p_2 = 2{\cdot}025;$

hence $Q/R = 9903$, or $Q_{SG} = 19{\cdot}8 \times 10^3$ cals. This value refers to 1 g.-mol. of vapour, and since we have found that the vapour is completely dissociated, it corresponds to 0·5 g.-mol. of ammonium chloride, so the value for 1 g.-mol. is $(Q_{SG})_{NH_4Cl} = 39{\cdot}6 \times 10^3$ cals., whereas Johnson found $37{\cdot}8 \times 10^3$ cals. and Braune and Knoke $39{\cdot}4 \times 10^3$ cals.

Also, from the same data, $C = 20{\cdot}5$, and hence the vapour-pressure formula is

$$2{\cdot}303 \log_{10} p = -9903/T + 20{\cdot}5$$

whence the sublimation temperature (for $p = 76$) is $T = 612{\cdot}3°$ (339·3° C.).

Summary.

Using the latest form of the densi-tensimeter and also its immediate predecessor, the authors determined the pressures and densities of moist, saturated ammonium chloride vapour, as a preliminary to studying the influence of intensive drying on these properties.

Vapour-pressure determinations showed that the heat of sublimation is not a temperature function within the range 254—353°, and the density determinations give the explanation of this behaviour, for they show the dissociation of the saturated vapour to be practically complete over the same range of temperature. Similarly, complete dissociation was found by using the extrapolation method previously described.

* The remarks of Braune and Knoke about the explanation of the behaviour of intensely dried ammonium chloride are incorrect. Our results with the moist material do not affect that explanation at all.

The authors conclude that the results of Smith and his collaborators, giving dissociations of about 60%, must be incorrect—probably for the same reason that their results for the vapour density of ammonium bromide are incorrect. The results of Braune and Knoke are in agreement with those of the authors.

The molecular heat of sublimation for 1 g.-mol. of ammonium chloride is calculated to be $39 \cdot 6 \times 10^3$ cals., and from the derived vapour-pressure formula the sublimation temperature is calculated as 339·3°.

THE UNIVERSITY, AMSTERDAM. [*Received, September 7th*, 1928.]

CCCLXXXVIII.—*Adsorption of Vapour on a Quartz or a Glass Wall.*

By ANDREAS SMITS.

SMITS and PURCELL (this vol., p. 2941) have shown that their "extrapolation method" enables one to find, not only the vapour density of the saturated vapour, but also the extent of adsorption by the walls of the apparatus. In the case of ammonium bromide, the change of the vapour-pressure curve of the saturated vapour into that of the unsaturated vapour (Boyle–Gay-Lussac curve) was not sharp, but took place over a temperature range of several degrees, *i.e.*, the saturated vapour-pressure curve was left at too low a temperature, and the Boyle–Gay-Lussac line was reached at too high a temperature. This continuous curve was found with both rising and falling temperatures, so there is no doubt as to its reality. Both quartz and Jena glass apparatus were used, and in order to keep the wall as smooth as possible, the apparatus had not been allowed to come into contact with water or water vapour.

These experiments were of great interest, since the results of McHaffie and Lenher (J., 1925, **127**, 1559) and of Lenher (J., 1926, 1785; 1927, 272) on the adsorption of water and benzene vapour on glass, silica, and platinum surfaces at temperatures near the saturation temperature had been criticised by Fraser, Patrick, and Smith (*J. Physical Chem.*, 1927, **31**, 897) on the ground that the walls of the apparatus were not plane, but had been etched by acid-cleaning. These authors had observed that for water and toluene the smoothness of the surface was very important, and that no adsorption of toluene on a plane surface could be detected by vapour-pressure determinations. At the time of publication of Fraser, Patrick, and Smith's paper, Rinse was completing investigations (this vol., p. 1442) in the author's laboratory which showed

that mercuric iodide was adsorbed in layers 500 molecules thick at 300°, even though the glass walls had been kept as smooth as possible and had not been in contact with water or water vapour. Still more recently, J. W. Smith (this vol., p. 2045) has shown that a platinum vessel, of which the walls had been amalgamated in order to render them as plane as possible, adsorbs molecular layers, the number of which increases as the saturation temperature is approached: within the range of 30° the maximum number of adsorbed molecular layers was 40 in the case of water and 300 in the case of benzene. Further, de Boer (*Physica*, 1928, **8**, 145) has found that even at room temperature 30 molecular layers of iodine are adsorbed on calcium fluoride, and if it had been possible to approach the saturation temperature more closely, this number would probably have been much higher.

The author's application of the extrapolation method to find the degree of adsorption by the glass wall has been mentioned (Smits and Purcell, this vol., p. 2943) but not yet described. In the paper quoted, Fig. 6 shows the continuous change of the saturated into the unsaturated vapour-pressure curve, and on extrapolation the two lines intersect at a point corresponding to 379° and 49 cm. Hg. The vapour pressure measured at this temperature was, however, 48 cm. Hg, *i.e.*, 1 cm. too low. The bulb of the apparatus had a radius of 5·25 cm., so the surface was 346·36 cm.^{2}, or say 350 cm.^{2}. The bulb contained 0·3404 g. of ammonium bromide, so the decrease of 1 cm. in the vapour pressure corresponded with 0·0068 g., *i.e.*, the number of adsorbed molecules is $4{\cdot}23 \times 10^{19}$. From X-ray investigations on ammonium bromide it follows that in a crystal layer a molecule has a cross section of 25×10^{-16} cm.^{2}. On a surface of 350 cm.^{2}, therefore, 14×10^{16} molecules can be arranged in one layer, but since $4{\cdot}23 \times 10^{19}$ molecules were adsorbed, the number of adsorbed molecular layers would be 300. This result is very remarkable and of the same order as that obtained by Rinse and by Smith.

Although this phenomenon is being further investigated in this laboratory with various surfaces and substances, the following points may already be emphasised. Suppose we have a bulb containing a liquid or a solid volatile substance, and adsorption occurs on the wall of the vessel, which is a general phenomenon; the system wall + adsorption layer will then be a part of the whole equilibrium system. Equilibrium cannot be established before the glass wall has adsorbed so many molecular layers that the vapour pressure of the "wall-phase" (as we may call it) is the same as that of the solid or liquid phase in the bulb. Now, the various experiments seem to show that, depending of course on the nature

of the substance, the wall-phase can consist of a large number molecular layers, and if we accept this conclusion, the followi considerations arise.

On increasing the temperature to the stage at which the last p of the solid or liquid phase has just disappeared, the wall-ph will still have a pressure equal to that of the saturated vapo at that temperature. Further increase of temperature causes t number of adsorbed molecular layers to become smaller and small If the solid or liquid phase had still been present, the number adsorbed molecular layers would have increased, so that now, t solid (or liquid) phase having disappeared, the number of adsorb molecular layers is too small to give a pressure equal to that the saturated vapour at the same temperature. The wall-pha will consequently give a lower vapour pressure, and the deficien will increase continuously with rising temperature.

Finally, the wall-phase disappears, leaving behind probably unimolecular layer, and the Boyle–Gay-Lussac line is practical reached.

Summary.

It is shown that experiments of other investigators and also the author indicate that the adsorption films on a mercury surfa and on glass or quartz surfaces, as plane as possible, formed almost saturated vapour, can consist of a large number of molecul layers.

THE UNIVERSITY, AMSTERDAM. [*Received, September 14th*, 1928.]

CCCLXXXIX.—*A Phase Rule Investigation of Cupr Bromide in Aqueous and Hydrobromic Aci Solutions.*

By SYDNEY RAYMOND CARTER and NORMAN JOSEPH LANE MEGSON.

APART from the desirability of acquiring accurate data for t solubility of copper bromide, a number of interesting problen arise concerning its hydrates and hydrobromides, as well as t remarkable colour effects which are observed in hydrobromic ac solutions containing cupric salts. From its heat of formatio Bodländer (*Z. physikal. Chem.*, 1898, 27, 61) has calculated t solubility of cupric bromide in water as 1·3 equivs. per litre, b this value, which presumably refers to ordinary temperatures, necessarily only approximate and has not yet been verified.

The salt is known in the anhydrous form and as a tetrahydrat

the former being obtained by evaporation of solutions on the water-bath, and the latter crystallising as green needles from solutions at about 0°; Kurnakow and Sementschenko (*Z. anorg. Chem.*, 1899, **19**, 337) give 29·0—30·5° as the transition temperature of the system. The tetrahydrate has no analogue in cupric chloride, the stable variety of which is $CuCl_2,2H_2O$. Löwig ("Das Brom und seine chemischen Verhältnisse," 1829) is said to have obtained $CuBr_2,2H_2O$ by evaporation of solutions of cupric bromide, but Berthemot (*Ann. Chim. Phys.*, 1830, **44**, 386), although usually credited with preparing greenish-yellow needles of the same salt, gives no analyses.

Cupric bromide gives a deep violet coloration with hydrogen bromide, which is attributed by Sabatier (*Compt. rend.*, 1894, **118**, 1260) to a hydrated hydrobromide; he prepared this salt in an unstable condition by passing hydrogen bromide into saturated cupric bromide solution, and although analysis gave $3CuBr_2,2HBr,6H_2O$, he considered that, owing to instability, it was really represented by $CuBr_2,HBr,2H_2O$. Dilution tended to destroy the colour, but if the dilution had not been carried too far heating restored it.

Other bromides (*e.g.*, those of potassium, sodium, calcium, and especially lithium) also give this colour with cupric bromide, and Kurnakow and Sementschenko (*loc. cit.*) have isolated a compound $CuBr_2,2LiBr,6H_2O$. Moreover, cupric chloride and sulphate give a similar colour reaction with hydrobromic acid.

Weinland and Knöll (*Z. anorg. Chem.*, 1905, **44**, 116) prepared black, hygroscopic needles, to which they assigned the formula $CuBr_2,HBr,10H_2O$, by leaving a solution of cupric bromide in 40% hydrobromic acid in contact with the product of the action of hydrogen bromide on molybdenum trioxide; if the molybdenum compound was omitted, cupric bromide was the sole product.

Since Foote (*J. Amer. Chem. Soc.*, 1923, **45**, 663), from a study of the system cupric chloride–hydrogen chloride–water, had found $CuCl_2,2H_2O$ to be the only stable solid phase at 25°, whereas at 0°, in high concentrations of acid, the compound $CuCl_2,HCl,3H_2O$ existed in addition, we undertook a similar study of the bromine analogues in order to gain information on the various points raised in the foregoing discussion.

EXPERIMENTAL.

Materials.—Cupric bromide was used in the anhydrous form, but since it was liable to contain a small percentage of cuprous bromide, it was purified by oxidation with hydrogen peroxide, or by recrystallisation.

$6N$; frequently, however, higher concentrations were required, i which case the gas was prepared by the action of bromine on solution of naphthalene in xylene (Kastle and Bullock, *Ame Chem. J.*, 1896, **18**, 105) and purified by red phosphorus suspende in concentrated hydrobromic acid. The purity of the gas w tested by repetition with it of several solubility determinatio already obtained by the use of the aqueous hydrobromic acid, an in all cases identical results were obtained.

Analytical Methods.—Copper was estimated volumetrically b titanous chloride, standard ferric alum and a large excess of 10 potassium thiocyanate being used as indicator. The latter co tained hydrochloric acid (about $1N$) to stabilise the cupric an ferric thiocyanates formed, as recommended by Emmett (J., 192 2059). Bromide was estimated by Volhard's method. Estimatio of the radicals in trustworthy specimens of cupric bromide we quite concordant, and showed that these methods were accura to within 1 part in 300 or 400 parts.

Solubility Apparatus.—In view of the high solubility of cupr bromide in water, it was desirable to use fairly small quantities solution. Accordingly, a solubility vessel was devised in whic the lower portion was narrow (2·5 cm. diameter; capacity 40 c.c. whilst the neck was wide enough to take a rubber bung carryi a mercury-sealed stirrer and a sliding glass stopper. A small gla cup was sealed on to the shaft of the stirrer to prevent groun glass and vaseline lubricant falling into the mixtures.

The sliding stopper was used for inserting a tube for the remov of the liquid-phase samples through small sintered-glass filter into either a pipette or a weighing bottle. The collecting apparat was suitably water-jacketed at the appropriate temperature whe necessary. An approximate density determination of the liqu was obtained at this stage by collecting a further sample in a sm pyknometer having a capacity of about 1·0 c.c. The solid pha was finally examined by draining away the remaining liquid a removing a specimen of the moist solid by a flattened glass spatul The solubility mixtures were usually stirred for 7—8 hours, a this period was shown to be ample for the attainment of equilibriu

The System $CuBr_2$–H_2O.

Solubility determinations (Table I) were made at a series temperatures ranging from 0° to 50°, the solid phase being examin in each experiment. The results are stated as g. of anhydro $CuBr_2$ per 100 g. of solution, and are shown graphically in Fig. 1.

Examination of these figures in conjunction with the gra shows two features of interest. (1) First, the solubility of cupr

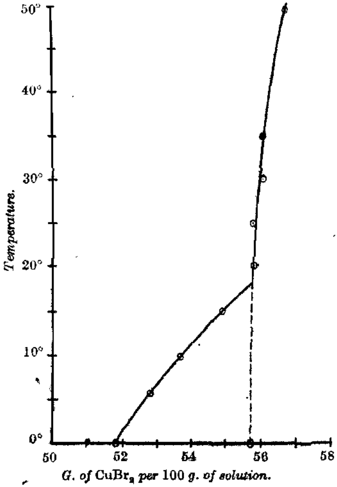
TABLE I.

Temp.	$CuBr_2$, %.	Appearance of solid phase.	Temp.	$CuBr_2$, %.	Appearance of solid phase.
0·0°	51·8	Green needles in deep brown liquid.	20·0°	55·9	Black rhomboids in deep brown liquid.
5·75	52·8		25·0	55·8	
9·9	53·7		30·1	56·1	
15·0	55·0		34·8	56·0	
			50·0	56·8	
			(*Metastable state*)		
			0·0	*55·7	

* This value was obtained by stirring only a slight excess of cupric bromide with water for $5\frac{1}{2}$ hours at 0°, a supersaturated solution being produced.

bromide is considerably greater than the value given by Bodländer (*loc. cit.*): the saturated solution has $d_{4^\circ}^{25^\circ}$ 1·84 (see below), giving the solubility of the anhydrous salt as 1030 g. or 9·2 g.-equivs. per litre. (2) Secondly, there is a distinct break in the curve between 15° and 20°, indicating some change in the solid phase present, and corresponding with the difference in crystalline form noticed under the microscope (see Table I).

FIG. 1.



It was considered that the green needles represented the tetrahydrate described by several workers (*e.g.*, Sabatier, *Bull. Soc. chim.*, 1894, **11**, 677). This was confirmed by draining and drying a sample as rapidly as possible at a low temperature. It was a bright olive-green solid (Found: $CuBr_2$, 75·85. Calc. for $CuBr_2,4H_2O$: 75·63%), darkening on keeping for a few days at room temperature.

On drying a sample of the black rhomboidal crystals on a porous tile and filter paper at room temperature, a solid was obtained

apparently identical with the anhydrous cupric bromide (Found $CuBr_2$, 99·9%). The lower portion of the curve therefore repre sents the solubility of $CuBr_2,4H_2O$ in water, whilst the upper portio gives the solubility of anhydrous $CuBr_2$. The latter is peculiar i that it has little or no temperature coefficient over the range 0—18—25°, and only a slight positive one from 35° to 50°.

The break in the curve at 18·0° obviously corresponds to th transition temperature of the hydrated salt; since this value i about 12° below that given by Kurnakow and Sementschenk (*loc. cit.*), various methods were adopted to substantiate it.

The Transition Temperature of $CuBr_2,4H_2O \rightleftharpoons CuBr_2 + 4H_2O$.

Experiments with the dilatometer indicated that the transitio temperature lay between 21° and 14°, but owing to considerabl supercooling, the method was unsuitable for more exact values.

A thermometric method gave more information, since the heatin and cooling curves exhibited breaks at 19·8° and 16·2°, respectively indicating a transition temperature of approximately 18°. Severa difficulties prevented this determination from being complete successful, however, the chief being the consistency of the solid which rendered efficient stirring almost impossible.

A more accurate value was obtained by using a modification o the thermometric method, due to Richards (*Z. physikal. Chem.* 1898, **26**, 690). A specimen of the tetrahydrate was prepared b intimately mixing 12 g. of the recrystallised salt with the theoretica amount of water (4 g.) and cooling the mass in ice with continuou stirring until it became nearly solid. The mixture was drained o porous plate, and allowed to dry in a closed vessel below 10°. Th hard green cake so produced showed the characteristic green needle of the tetrahydrate under the microscope, and since analysi indicated almost 100% of that salt, it was used without furthe purification.

About 12 g. of this salt were introduced into a test-tube fitte with thermometer and glass stirrer, and contained in a wider tube leaving an annular air space of about 3 mm. The whole wa placed in a water-bath at 19·5°, and the inner tube removed an dipped in the warm water until partial melting of the content occurred; it was then wiped dry, replaced in the jacket, an allowed to stand in the bath. On stirring, the temperature of th mixture fell from 18·5° to 17·97°, where it remained constant fo 45 minutes. It then rose slowly to 18·08° after falling to 17·90° and finally fell with the temperature of the outer bath. The valu 17·97° was therefore taken as the transition temperature of th system.

No evidence was found to support the existence of $CuBr_2,2H_2O$ either microscopically or from an examination of the solubility curve. The published analyses of this substance by previous authors were possibly carried out on samples of $CuBr_2,4H_2O$ which had effloresced.

The System $CuBr_2$–HBr–H_2O *at* 25°.

This system was investigated in the hope of elucidating the constitution of the compound prepared by Sabatier (*Compt. rend.*, 1894, **118**, 1260), and also of obtaining some evidence as to the cause of the violet colour produced by strong hydrobromic acid solutions and copper salts.

Various mixtures of hydrogen bromide in water were stirred with cupric bromide for 7—8 hours in the solubility bottle at 25°, and samples of the liquid phase and of the moist solid were then collected and analysed, the results being given in Table II and plotted

TABLE II.

Mixture.	$d_{4°}^{25°}$	Liquid phase. CuBr$_2$, %.	HBr, %.	Moist solid phase. CuBr$_2$, %.	HBr, %.	
1	1·84	55·8	—	100	—	
2	1·82	52·3	2·9	80·8	1·4	*
3	1·78	48·3	6·3	—	—	*
4	1·73	43·2	10·6	81·8	3·8	*
5	1·69	37·6	15·4	—	—	*
5*a*	1·68	37·0	15·8	81·5	5·0	*
6	1·65	32·9	19·4	82·2	5·1	*
6*a*	—	32·8	19·7	—	—	*
7	1·63	26·9	26·0	69·1	10·9	*
8	1·64	25·9	26·9	76·7	8·4	†
9	1·65	23·1	31·9	73·6	11·3	‡
10	1·68	22·2	34·6	—	—	‡
10*a*	1·68	21·8	35·0	75·1	11·0	‡
11	1·72	20·4	39·1	78·4	10·6	‡
12	1·74	19·2	42·1	75·4	12·6	‡
13	—	18·5	43·6	62·3	19·8	‡
14	1·79	15·8	48·0	79·4	11·1	‡
15	—	15·1	48·8	—	—	‡
16	—	11·8	53·5	58·9	25·1	‡
17	—	10·8	54·7	—	—	‡
18	1·83	7·7	59·3	51·4	30·7	‡

Mixtures 1—7 have α-$CuBr_2$ as the stable solid phase.
Mixtures 8—18 have β-$CuBr_2$ as the stable solid phase.

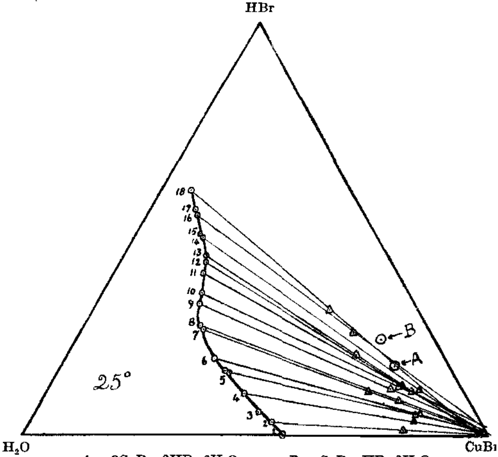
* Under the microscope the solid phase appeared as black rhomboids.
† Under the microscope the solid phase appeared as rhomboids mixed w much amorphous solid.
‡ Under the microscope the solid phase appeared as small, black, n crystalline particles.

aphically in Fig. 2. From the compositions of the moist residu ose of the pure solid phases were deduced by Schreinemake

method (*Z. physikal. Chem.*, 1893, **11**, 76), and the experiment values all pointed consistently to anhydrous cupric bromide as tl solid in equilibrium throughout the whole range of acid solutions.

In order to obtain solubilities in high concentrations of acid, saturated solution of hydrogen bromide at 25° was prepared by tl method previously described. Attempts were made to move sti further along the curve by passing hydrogen bromide into variou

FIG. 2.



$A = 3CuBr_2,2HBr,6H_2O$. $B = CuBr_2,HBr,2H_2O$.

solutions of aqueous cupric bromide, but these were only successfu in special circumstances. When these high concentrations of aci were being dealt with, much fuming took place, and as a precautio water was initially placed in both weighing bottles to prevent los of the gas from the samples of phases extracted.

The solubility of the cupric bromide is seen to diminish wit an increasing concentrations of hydrobromic acid, falling from 55·8% 17·97% with increase of acid from 0% to 59·3%. The solubilit system shows only one break (at Mixture 7), and the solid phase i m with the solution is in every case pure cupric bromide

The latter fact had already been foreshadowed for low concentrations of acid by the results from the two-component system.

The density of the solution shows no marked break, but on the other hand has a definite minimum. It descends smoothly from 1·84 to 1·63, then rises regularly again to 1·83. Mixture 7, where the break in the curve occurs, in addition to possessing the minimum density of 1·63, has other important features of interest, first, in relation to the colour of the solution, and, secondly, in connexion with the form of the solid phase.

(1) When hydrogen bromide was introduced in small quantities into the deep brown saturated solution of the copper salt, a violet tinge was imparted to the solution, gradually increasing in intensity with rise in concentration and masking the brown colour. When the concentration of the acid indicated by Mixtnre 7 was reached, all traces of brown disappeared, and the solution assumed a bright violet colour, which persisted in an intensified degree with increase of acid. In thick layers, these solutions were almost opaque.

(2) *Microscopic examination* of the solid phase at low concentrations of hydrogen bromide showed black, rhomboidal crystals in a brown or violet-brown solution. These persisted in concentrations of acid up to 26% (Mixture 7) and to a small extent to Mixture 8, after which no definite crystalline form for the solid could be obtained, in spite of many attempts.

Since, throughout the curve, the stable solid phase is anhydrous cupric bromide, it seems probable that the break at Mixture 7 must correspond to a change in the form of that salt. For convenience, these two forms may be designated α-$CuBr_2$ and β-$CuBr_2$ the former being crystalline, and the latter existing in a non-crystalline form in high concentrations of hydrobromic acid.

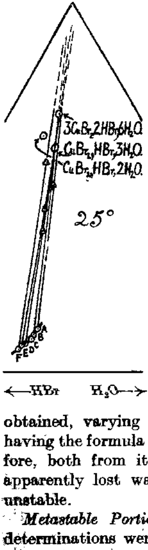
The Different Forms of Cupric Bromide and the Colours of their Solutions.—It will be noted that the ranges of existence of the brown and of the violet-coloured solutions coincide approximately with the ranges of existence of the α- and β-salts respectively, and it might be thought that the violet coloration is associated in some way with the β-form. The coincidence may be merely accidental, but, on the other hand, it is well known that a change in the solid phase leads to a distinct change in the physical properties of the saturated solution in equilibrium with it. There are very few data in other systems to test whether this principle holds in the case of modifications of the same substance with regard to the colour of their solutions, but it may be mentioned that the various acid ferric phosphates are associated with solutions having different colours (J., 1923, **123**, 2231).

The changes in colour which salt solutions undergo as the result

of alteration of temperature or the addition of acids or other sa have been extensively studied by Donnan, Sidgwick, Ostwald, a others (for references, see J., 1910, 97, 957), and they can usua be explained by considerations of hydration, ionisation, or compl formation.

The Possibility of Complexes of Cupric Bromide and Hydro Bromide.—Since one of our main objects was the investigation the possible solid phases, we thought it interest to seek evidence of complex acid sa which might exist in the solid state. Exam ation of the solubility curve shows no indicati of a stable solid phase having either of t formulæ put forward by Sabatier to represe the composition of the compound prepar by him (see points A and B, Fig. 2). attempt was made to repeat his experime of passing hydrogen bromide into a saturat solution of cupric bromide, and the mixtu was allowed to cool before being stirred in t thermostat. A modification was also int duced by cooling the solution during the act passage of the gas. In each case, after stirri for 7—8 hours, the points obtained lay on t solubility curves (14, 16, and 17) and h anhydrous cupric bromide as their stable so phase.

FIG. 3.



Attempts were also made to obtain analy before stirring, by draining samples of t solid immediately after preparation by t above method, in a closed vessel, until app ently dry. Very inconsistent results w obtained, varying from practically pure $CuBr_2$ to a compou having the formula $CuBr_2,HBr,3H_2O$. The substance seemed, the fore, both from its appearance while draining (during which apparently lost water) and from the analysis, to be extrem unstable.

Metastable Portion of System $CuBr_2$–HBr–H_2O *at* 25°.—So determinations were carried out by stirring mixtures obtained above for short periods of from 1—4 hours at 25° in the hope gaining evidence of a complex solid phase before the latter l time to break up. Table III and Fig. 3 illustrate the resu obtained in these circumstances, the solid phase appearing un

TABLE III.

Mixture.	$d_{4°}^{25°}$.	Liquid phase.		Moist solid phase.	
		$CuBr_2$, %.	HBr, %.	$CuBr_2$, %.	HBr, %.
A.	1·81	15·3	49·5	52·6	27·0
B.	1·83	14·1	51·1	52·0	28·8
C.	1·83	13·0	52·4	—	—
D.	1·83	11·9	54·3	41·1	36·0
E.	1·83	11·5	55·3	46·7	32·9
F.	1·87	10·4	56·7	58·5	26·6

It will be seen from the figure that the tie-lines through the moist solid phases focus probably on the compound

$$3CuBr_2,2HBr,6H_2O.$$

The complex is certainly not $CuBr_2,HBr,2H_2O$, as suggested by Sabatier, although it is possibly $CuBr_2,HBr,3H_2O$; if this were so, it would correspond to the analogous compound, $CuCl_2,HCl,3H_2O$, described hy Foote (*loc. cit.*). Evidence that one of the above formulæ really represents the composition of the solid phase is afforded by the fact that the moist solid phase gives points much farther from the apex of the triangle than do moist specimens of cupric bromide alone.

The mixtures themselves lie on a smooth curve, of which the relationship to the main curve (Fig. 2) will be seen from Fig. 4, where a portion of the triangular diagram is drawn to a larger scale; being on the right of the main curve, *i.e.*, nearer the solid phase, this curve must represent the more unstable form. In addition, from the position of the curve subsequently obtained at 0° (shown in Fig. 4), increase of temperature would appear to favour the stability of the compound, which was always destroyed after continued stirring for 7—8 hours at 25°, even in concentrated hydrobromic acid solution.

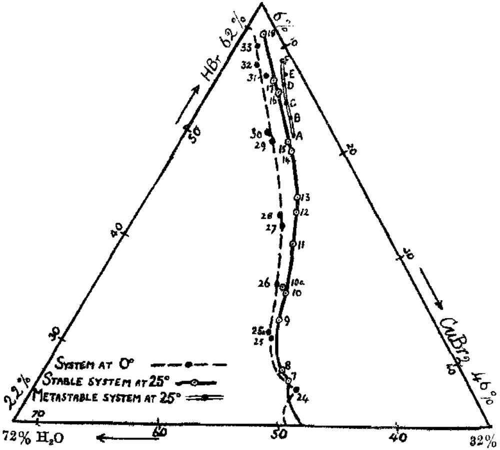
In this connexion it is of interest to notice that combination between cupric bromide and soluble bromides is already suspected to occur in solution, and the existence of the resulting complex ions has been detected by Denham by migration experiments (*Z. physikal. Chem.*, 1909, **65**, 641; J., 1919, **115**, 1269). The presence of such complex compounds or their resulting ions may be advanced as an alternative explanation of the violet coloration of cupric bromide in hydrobromic acid solutions. If this were the case it would be in agreement with an observation of Sabatier

of solid phases in equilibrium with them : a study of the solution themselves would be necessary for a complete explanation.

The System $CuBr_2$–HBr–H_2O *at* 0°.

The system at 0° was investigated in a very similar way to tha used at 25°, although some of the experimental details were slightl modified. The temperature of the thermostat was maintaine constant by a mixture of water and crushed ice. The liquid phas

FIG. 4.

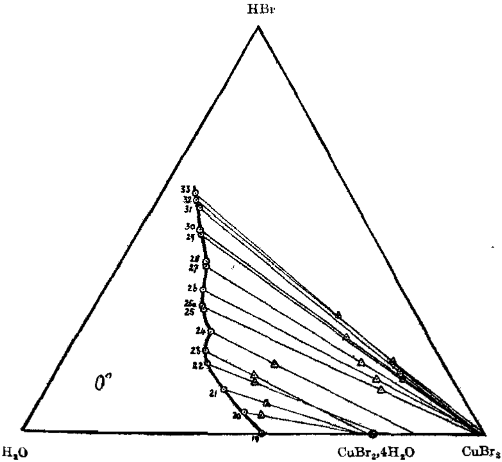


was extracted by means of the apparatus previously employed, but it was necessary to jacket the filter with ice-cold water. The solid phase was removed precisely as before, but it was found impracticable to carry out density determinations at 0°, partly by reason of the viscous nature of the solutions. For low concen trations of acid, it was deemed advisable to inoculate mixture with a crystal of $CuBr_2,4H_2O$ after 2—3 hours in the solubility vessel, for otherwise, even after 7—8 hours there was considerabl risk of supersaturation occurring, and of anhydrous bromide being left as the stable solid phase. Table IV and Fig. 5 summarise th

TABLE IV.

Mixture.	Liquid phase. CuBr₂, %.	Liquid phase. HBr, %.	Moist solid phase. CuBr₂, %.	Moist solid phase. HBr, %.
19	51·8	—	75·85	—
20	45·6	5·1	49·4	4·8
21	38·1	10·9	49·3	7·3
22	31·3	17·5	43·9	12·9
23	29·4	20·3	43·1	14·5
24	28·0	25·1	45·9	17·4
25	23·6	30·4	—	—
25a	23·2	30·7	71·9	11·2
26	21·3	35·2	69·8	13·5
27	18·8	41·2	64·5	17·8
28	18·2	42·0	—	—
29	13·8	49·0	75·4	13·8
30	13·2	49·7	58·0	24·0
31	10·1	55·4	73·6	15·5
32	8·4	56·9	53·5	29·3
33	7·7	58·8	71·1	18·2

FIG. 5.



As with the curve at 25°, this system at 0° shows a sharp discontinuity, but in this case it is due to the solid phase changing from the tetrahydrate to the anhydrous salt. Mixture 24 is at the break and all points before that have the hydrated salt as their stable solid phase. It has already been determined for Mixture 19 that $CuBr_2,4H_2O$ is the stable phase at 0°. Addition of hydrobromic acid causes a lowering of the melting point of the hydrate,

i.e., it lowers the transition temperature. Hence, when sufficient acid has been added, the transition temperature falls to below 0°, and anhydrous cupric bromide becomes the only stable form.

Microscopic examination of the solid phase for Mixtures 19—22 showed green needles in a violet-brown or brown solution. Mixture 23 showed very few needles, for these decomposed with the heat of the room, their transition temperature probably being 3—4° in the prevailing concentration of acid: they could actually be seen decomposing and producing the characteristic black rhomboids of anhydrous bromide. Mixture 24 is peculiar, in that microscopic examination revealed only rhomboidal crystals, whilst the tie-line through its moist solid phase falls between $CuBr_2$ and $CuBr_2,4H_2O$, indicating that this point is at the junction of the two curves. Both solids are capable of existence here, but owing to temperature difficulties, the hydrate was not sufficiently stable to be seen. From Mixture 25 onwards, the only stable solid phase present was anhydrous cupric bromide; from its appearance under the microscope, it must have been the non-crystalline β-variety.

When the hydrobromic acid concentrations are increased, the cupric bromide solutions at 0° exhibit a sequence of colour changes from brown to violet which are similar to those observed at 25°. It is noteworthy that at high concentrations of acid (*i.e.*, in the region of the violet solutions) the same solid phase (β-$CuBr_2$) persists at both temperatures, whilst in the low acid concentrations (brown solutions) the solid phases at 25° and 0° are α-$CuBr_2$ and $CuBr_2,4H_2O$, respectively. No evidence of the formation of any ternary complex compound at 0° was obtained from the curve.

The general temperature relationships of the curves at 0° and 25° may be judged by an examination of Fig. 4. Over the greater part of the system, cupric bromide evidently possesses a positive temperature coefficient of solubility, and this is still more marked when $CuBr_2,4H_2O$ becomes the stable phase at 0°. In the neighbourhood of Mixture 24, however, on the curve at 0°, the curves cross, indicating that in this region the solubility of the salt in hydrobromic acid decreases with rise of temperature. There can be little doubt of the accuracy of the observation, since Mixtures 28, 27, 26, and 25 all tend towards the curve at 25°, but the region has not been investigated experimentally in greater detail.

Summary.

1. The solubility curve of the system $CuBr_2$–H_2O has been investigated over the range 0—50°, one of two solid phases, $CuBr_2,4H_2O$ and $CuBr_2$, being found according to the temper-

2. The transition temperature has been determined as 18·00° ± 0·05°.

3. The solubility curve of the system $CuBr_2$–HBr–H_2O at 25° shows only a solid phase of anhydrous $CuBr_2$. There are two forms—α-$CuBr_2$, which has well-defined rhomboidal crystals, and β-$CuBr_2$, which is non-crystalline. The break between the two forms occurs at 26% of HBr.

4. A metastable portion of the system at 25° has been investigated and found to possess as its solid phase a complex compound of the probable formula $3CuBr_2,2HBr,6H_2O$, the stability of which is probably favoured by increase of temperature.

5. The system $CuBr_2$–HBr–H_2O has been investigated at 0°, and the solubility curve found to exhibit a break corresponding to the two stable phases $CuBr_2,4H_2O$ and β-$CuBr_2$.

6. The characteristic colour changes of cupric bromide in hydrogen bromide solutions have been discussed in the light of this investigation.

7. No evidence has been obtained of the existence of $CuBr_2,2H_2O$ in any of the systems studied.

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CCCXC.—*Studies in the Composition of Coal. The Rational Analysis of Coal.*

By WILFRED FRANCIS and RICHARD VERNON WHEELER.

A RATIONAL analysis of any coal can be given in terms of the proportions of free hydrocarbons, resinous compounds, organised plant entities, and ulmin compounds that it contains (see, *e.g.*, Cockram and Wheeler, *J.*, 1927, 700), for these are the principal ingredients of the coal substance and they have characteristic properties. Such an analysis is not sufficient, however, to specify completely the quality of the coal, for the ulmin compounds, of which it is mainly composed, are not identical in character in all coals. We have, in fact, shown (J., 1925, **127**, 2236) that the properties of the ulmin compounds, which exist in all coals, from lignites to anthracites, are modified by progressive changes in molecular arrangement. When first formed by the decay of vegetable tissues, the ulmins are readily soluble in alkaline solutions, but the further the "coalification" of the material proceeds the less is its natural content of soluble ulmins and the less easily can such ulmins be "[illegible]" by oxidation processes (see *Safety in Mines Research*

Coals can differ from each other in respect of (1) the proportion and (2) the properties of their ingredients. There is sufficien evidence, which cannot be detailed here, that the chemical com positions of the free hydrocarbons, resinous compounds, and organ ised plant entities (*e.g.*, spore exines and cuticular tissues) do no vary much whether those bodies form part of a lignite, a bituminou coal, or a semi-anthracite. Certainly they do not vary sufficienth to account for the wide differences in properties of such coals. Or the other hand, the composition of the ulmin compounds does vary widely, dependent upon the coals from which they are obtained by reason of differences both in the external groupings of the large and complicated molecule and in its internal, or nuclear structure.

A preliminary study of a series of coals suggested that a measure of the difference in character as between the ulmin compounds of two coals could be obtained by determining their reactivity; for example, as regards oxidation, from the proportion rendered soluble in alkalis after their subjection to limited oxidation under standard conditions. Such a measure, a "reactivity index" for the ulmins, should be sufficient, in addition to a rational analysis, to specify a coal so that its general properties would be discernible.

We have tested this suggestion by the examination of a series of coals from the same seam, the Pittsburgh seam of the United States of America. Some of the samples were obtained through the courtesy of Dr. David White, of the U.S. Geological Survey, who himself collected them; others were collected by one of us in person. The advantage of carrying out a study of this kind on coals from the same seam lies in the elimination of a possible complication due to wide differences in character of the vegetation from which the coals were formed.

The Pittsburgh seam extends conformably over wide areas in Pennsylvania, Ohio, West Virginia, and Maryland, and the coal varies in carbon content from 78% at its westernmost limit, where it is a sub-bituminous coal (Seyler's ortho-per-lignitous) to 90% in the Georges Creek region of Maryland, where it is a semi-anthracite (Seyler's sub-meta-bituminous). When the coal measures of the Allegheny formation were deposited, there existed over these areas a vast coastal plan, or an area of subsidence, upon which a series of almost continuous stretches of vegetation accumulated, each in turn to be gradually covered by detrital matter carried by the encroachment of water (see White, Bull. 38, *U.S. Bureau of Mines*, 1913). The Pittsburgh seam, which lies above the coals of the Allegheny formation, was formed under similar conditions. The

nainly to changes in temperature and pressure caused by earth novements during the coalification process.

In addition to the Pittsburgh seam, coals were collected from he lignite fields of Montana, North Dakota, and Wyoming, from he bituminous fields near Price, in Utah, and from the Yampa 'alley in Colorado, where local earth movements have transformed oals of comparatively recent formations into semi-anthracites. Vith the coals of the Pittsburgh seam, the earth movements responsible for their regional metamorphism were those resulting 1 *the Allegheny mountains, the greatest upheavals* being in the ieorge's Creek district of Maryland (*e.g.*, the Ocean coal) and the east in Ohio (*e.g.*, the Bailey's Mills coal). In Montana and North)akota, the eartb movements which caused the change of rank of 1e coals were those which formed the Rocky Mountains. In laces where the uplift of the mountains was not felt, as in North)akota, the coal is a lignite. There is a general tendency for the ink of the coal to increase in a westerly direction (toward the ocky Mountains), whilst it is highest in the neighbourhood of ocal upheavals.

The method of examination, in addition to the usual forms of nalysis and the determination of the proportions of the principal igredients, has been to measure the reactivity with oxygen of the lmin *constituents*. This has been done both directly, from the mount of oxygen combining with them in a given time, and idirectly from the rate of production of alkali-soluble ulmins nder standard treatment with an oxidising agent. It has been und that the order of reactivity of the ulmins as measured by ich method is substantially the same. In Table I the rational ıalyses of the coals examined are recorded, together with their rbon contents. A " reactivity index " for the ulmins (obtained s described in the experimental part of this paper) is also included, nd the coals are arranged (those of the Pittsburgh seam being rouped together) in two groups of decreasing reactivity.

In the rational analyses, the hydrocarbons and resins have been rouped together. These are oil-yielding constituents of high ydrogen content, and their presence in the coal in suitable amount fects (but is not wholly responsible for) its coking power. There no general relationship between the quantity of hydrocarbons nd resins extractable from a coal and its age or degree of coalificion; nor is this to be expected, since the concentration, in the iginal coal-forming materials, of the substances that yielded iem must have been to a certain extent accidental. Their quality

TABLE I.

Rational Analyses of Coals.

	Name of coal.	Rational analysis, %. Hydrocarbons and resins.	Organised plant entities.	Ulmins.	Reactivity index of ulmins.	Carbon, %, on ash-free, dry coal.
Pittsburgh Seam (Carboniferous).	Bailey's Mills*	5·4	8·7	85·9	61·5	78·9
	Skillcross	3·1	9·7	87·2	58·8	81·1
	Elm Grove	6·4	7·6	86·0	56·7	81·1
	Monongah†	5·0	10·3	84·7	47·0	83·3
	Irwin	3·9	8·0	88·1	45·0	84·5
	Revere*	3·5	9·2	87·3	42·5	86·1
	Greensburg	4·5	15·3	80·2	41·5	86·7
	Trotter	3·7	15·1	81·2	39·6	87·6
	Revere†	7·8	10·4	87·3	31·2	85·2
	Martin	7·4	13·0	79·6	30·2	84·8
	Scotch Hill	4·4	8·7	86·9	29·2	85·2
	Berkley	1·0	13·8	85·2	20·0	87·6
	Jamison	3·2	8·8	88·0	16·0	86·5
	Vogele†	2·3	13·3	84·4	14·0	86·6
	Vogele*	1·6	2·7	95·7	12·0	87·4
	Seal†	2·7	12·5	84·8	10·0	89·1
	Ocean*	<1	9·5	89·5	5·0	89·0
Tertiary and Cretaceous.	Wyodak	3·8	5·1	91·1	80·0	71·9
	Wadge	4·9	14·4	80·7	71·2	78·4
	Hotchkiss	3·4	1·3	95·4	70·0	73·4
	Milk River	3·8	3·8	92·4	68·5	73·4
	Pinnacle	4·1	12·4	83·5	55·3	79·1
	Owl Creek	3·7	5·3	91·0	54·3	77·0
	King	5·7	7·0	87·3	53·2	80·7
	Gantar	4·0	9·2	86·8	52·1	78·4
	Colstrip	2·2	11·5	86·3	50·5	74·6
	Castlegate	5·8	11·6	82·6	49·0	81·5
	Sunnyside	5·7	4·0	90·3	48·0	82·5

* Bottom part of seam. † Top part of seam.

They remain soluble in organic solvents, for example, except in that part of the seam that has been subjected to extreme tectonic disturbance, as in the Westmoreland and Somerset Counties of Pennsylvania and the George's Creek region of Maryland. In the samples obtained from these regions (the Vogele, Berkley, and Ocean Mines, Table I), the proportions of chloroform-soluble material have greatly diminished, and it can be assumed that the effects of the violent earth movements have been either to remove part of the hydrocarbons and resins (by distillation) or to render them insoluble.

Similarly, there is no connexion between the degree of coalification of the seam and the proportion of organised plant entities that it may contain. In the Pittsburgh seam the proportions of these bodies (which other researches have shown to be extremely resistant to decay and to the processes of coalification) vary at haphazard between 3 and 16%, dependent no doubt, as with the

resins, on their original, accidental, concentration in the coal-forming materials. The spore exines and cuticular tissues, which form the bulk of the morphologically organised plant entities, are of high hydrogen content and are oil-yielding constituents of the coal, the oils consisting mainly of paraffins and unsaturated hydrocarbons.

Regarding these non-ulmic organic constituents as impurities, it is desired to trace a relationship between the "reactivitics" of the ulmin constituents and the chemical compositions of the coals as determined by ultimate analysis. It will be understood that, since the proportions of the non-ulmic constituents, of higher hydrogen content than the bulk of the coal, vary between rather wide limits (4·6—23·2% in the Pittsburgh seam), any such relationship can only be partial. The percentage of carbon, being high throughout the series of coals, should be least affected by the presence of varying quantities of materials of high hydrogen content. Table I shows that there is, in fact, a general relationship between the carbon content of the coal as a whole and the "reactivity" of the ulmins it contains, a relationship which is remarkably close when, in addition to the fact that the ultimate analysis shows no more than the mean carbon content of all the organic constituents of the coal, it is remembered that the accuracy of coal analyses, calculated, as is usual, on an ash-free, dry basis, suffers from the fact that the inorganic impurities differ in composition and amount from the ash they yield on incineration. For these reasons we consider the "reactivity index" of the ulmins to be a better measure of the degree of coalification than the carbon content of the coal as a whole can be, though the latter may often be a sufficiently close measure. For example, if care be taken to choose only the vitrain portion of a seam, the fact that this portion can readily be freed from all but a small percentage of mineral matter and is essentially free from spore exines and cuticles, causes the analysis to be nearly representative of the ulmin constituents alone. Thus, in Table II a comparison is made between the carbon contents of four coals and those of the vitrains separated from them. It will be seen that the "reactivity index" of the ulmins corresponds with the carbon content of the vitrain from the coal rather than with that of the coal as a whole.

What we have termed the "degree of coalification" of a coal is sometimes (following David White, *e.g.*, *U.S. Bureau of Mines*, Bull. No. 38, 1913) termed its "rank," a coal of lowest rank being one in which the processes of coalification (in whatever way induced, *i.e.*, whether by time, temperature, or pressure) have had least

TABLE II.

Name of coal.	Carbon contents, %, on ash-free, dry coal. Coal as a whole.	Vitrain portion only.	Reactivity index of ulmins.
Trotter	87·6	85·4	39·6
Revere (bottom) ...	86·1	85·9	42·5
Revere (top)	85·2	86·5	31·2
Jamison	86·5	87·2	16·0

been the most effective. We have shown elsewhere (*loc. cit.*) that the external groupings of the ulmin molecules are modified with increasing rank of the coal. The present work affords additional evidence of this. From the results in Table III, which records the amounts of oxygen that combined with the coals at 150° (one method of determining the reactivity of the ulmins), it will be seen that the ratio between the oxygen that remained combined with the coal and the total consumed increases as the rank of the coal increases. In order that a given quantity of oxygen shall combine with an ulmin of low rank (forming acidic groupings), a greater total quantity must be consumed than with a high-rank ulmin, presumably because the nuclear groupings of the ulmin molecule of low rank are of smaller mass in comparison with that of the external groupings. These external groupings are the first points of attack by the oxygen (yielding water and oxides of carbon), and they confer high reactivity on the low-rank ulmins.

As the rank of the ulmins increases, the amount of oxygen that must combine with them, forming acidic groupings which confer on them solubility in alkaline solutions, also increases, whilst the ratio C : O in the soluble ulmins produced becomes greater (see Tahle III). This suggests that the nuclear structure of the ulmin molecules increases in magnitude with their rank, and that polymerisation or condensation takes place during the coalification process.

An important inference to be drawn from the examination of the Pittsburgh seam is that all coal ulmins which have the same "reactivity index" are alike in constitution and properties. Exceptions are apparent amongst coals of younger formations, explicable by reason of the widely distant geological periods during which the coal-forming materials accumulated, but there seems no reason why coals from the upper (and, perhaps, the middle) carboniferous period should differ materially in character from those of the Pittsburgh seam. For any such coal, a determination of the "reactivity index" of the ulmins, together with an estimation of the principal ingredients, should give more valuable information as to its properties than other forms of analysis. We are accumulating such data with regard to a number of British coals

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EXPERIMENTAL.

For convenience, the coals are identified by the name of the mine at which the seam is worked. The positions of the mines are recorded in Table VI. The Pittsburgh seam varied in thickness from 4 to 10 ft., the others from 6 to 80 ft. With few exceptions (recorded in Table I), the samples, of about 10 lb. weight, were taken from the middle of the seam at a newly-exposed face. The blocks of coal were immediately wrapped in sheets of lead foil to prevent exposure to the air. In the laboratory, the coarsely ground samples were dried in a vacuum oven and extracted with pyridine in large Soxhlet apparatus in an atmosphere of nitrogen, and the γ_1- and γ_2-fractions separated by treatment with chloroform. The α- and β-compounds were then dried in a vacuum at 105°, ground, and sieved. All the oxidation experiments were made on samples so treated.

Rate of Oxidation.—To determine the rates of oxidation of the samples, 10 g. of each, sieved so as to pass a 100- and remain on a 200-mesh sieve (Tyler U.S. standard), were placed in glass tubes in a constant-temperature oven at 150°, and pure dry air was drawn through them for several weeks. The time taken for complete conversion of the coal ulmins into alkali-soluble compounds varied with the character of the coals, being as long as 40 weeks for those of highest carbon content. The quantities of water and oxides of carbon formed during the reaction were measured, as well as the changes in weights of the coals. The amounts of oxygen that remained combined with the residues, and the total oxygen consumed, could thus be estimated. The results for the first two weeks are recorded in Table III, the amounts of oxygen being expressed in c.c. per g. of ulmins free from unoxidisable plant entities and mineral matter.

So far as the coals of the Pittsburgh seam are concerned, their carbon contents follow closely the rates of oxidation of the ulmins, but amongst the other coals there are notable exceptions. For example, the ulmins of Colstrip coal react with less oxygen in a given time than do those from Wadge coal, though the carbon content of the former coal is the lower by 4%. There are possibilities of experimental error with such low-rank coals, both in the analyses, because of their high moisture contents, and in the measurements of rates of oxidation, because their avidity for oxygen might cause them to absorb appreciable quantities during their preliminary treatment. From superficial examination of these coals, however, one would judge the Colstrip to be of lower rank than the Wadge,

TABLE III.

Atmospheric Oxidation.

Volumes of oxygen consumed (c.c. per g. of coal ulmins). Temp., 150°.

Name of coal.	After 1 week. Total consumed.	After 1 week. Combined with coal.	After 2 weeks. Total consumed.	After 2 weeks. Combined with coal.	Analysis of soluble ulmins. C, %.	Analysis of soluble ulmins. H, %.
Bailey's Mills	273	89	352	109	63·2	3·1
Skillcross	243	72·5	319	95·5	—	—
Elm Grove	236	89	310	109	63·1	3·5
Monongah	228	83·5	305	104	63·6	3·3
Delmont	228	67	298	88	—	—
Greensburg	202	68	266	88	68·1	3·0
Martin	198	72	258	88·5	69·5	3·0
Revere (bottom)	196	67	264	90	68·6	3·0
Scotch Hill	194	67	261	86·5	66·3	3·3
Revere (top)	193	58	—	—	67·7	3·3
Trotter	193	58	256	78	68·9	2·8
Jamison	190	67	246	86	70·2	3·4
Vogele (top)	152	72	222	106	69·6	2·9
Berkley	146	49	203	69	71·9	2·9
Seal	137	50	196	74·5	72·1	2·9
Vogele (bottom)	136	59	193	78·5	—	—
Ocean	79	36	120	45·5	72·6	2·9
Wyodak	331	69·5	411	71·5	60·8	2·9
Knife River	320	54	390	68	63·5	3·0
Milk River	308	65	372	67·5	59·7	2·9
Wadge	285	71	391	97·5	62·7	3·0
Hotchkiss	274	52·5	327	55	61·5	3·1
King	264	70	344	80·5	63·4	3·0
Pinnacle	262	65	388	97	—	—
Colstrip	259	64	356	88·5	62·0	3·0
Gantar	259	78·5	335	93·5	62·1	3·0
Castlegate	259	84	347	109	65·2	2·0
Sunnyside	254	60	327	75	65·6	3·1
Owl Creek	245	66	327	73	61·2	2·9

Rate of Formation of Soluble Ulmins.—(a) *By atmospheric oxidation.* Samples were exposed in thin layers in an air-oven at 150° for several weeks. At the end of each week 1 g. of each was withdrawn and extracted during ½-hour with 150 c.c. of a boiling 1% potassium hydroxide solution. The solutions were filtered while hot, and the ulmins precipitated by hydrochloric acid, filtered through tared papers, washed, dried, and weighed.

The results are recorded in Table IV. In order to compare the reactivities of the coals, it is convenient to calculate the times taken for 50% production of soluble ulmins, figures readily obtainable from the data recorded with an accuracy within 1%. The coals are arranged on this basis in Table IV in order of decreasing activity. The order is substantially the same as that given by their rates of oxidation (Table III), and it will be noticed that

Gantar), which were there placed low in order of reactivity (for their carbon contents) are again so placed.

One marked discrepancy between Tables III and IV is caused by the Knife River coal, which was one of the youngest studied. In appearance it resembled dark brown wood, the seam containing complete tree trunks. When mined, its content of soluble ulmins was 24%, but on drying at 104° this was reduced to 4% (despite the fact that about 35% of moisture was driven off). Even this moderate temperature, therefore, caused either dehydration or condensation of the ulmin molecules, an effect which heating in air at 150° would no doubt intensify, despite the fact that soluble ulmins were simultaneously formed by oxidation. With such coals the rate of formation of soluble ulmins during atmospheric oxidation cannot be used as a measure of their rank.

TABLE IV.

Atmospheric Oxidation.

The rate of formation of soluble ulmins.

Time in weeks	Percentage formation of soluble ulmins. 1	2	3	4	6	8	10	11	Hours required for 50% formation.
Name of coal									
Bailey's Mills ...	—	31·5	77·5	—	100	—	—	—	390
Skillcross	17	31	76	—	—	100*	—	—	395
Elm Grove......	—	30	75	—	100	—	—	—	410
Monongah	—	24·5	72	—	100	—	—	—	425
Delmont.........	—	27·5	57·5	76	100	—	—	—	430
Greensburg ...	—	27	57	—	—	100	—	—	475
Trotter	—	26·5	54	75	100	—	—	—	480
Martin	—	20	52·5	—	—	100	—	—	495
Revere (bottom)	—	22	51	—	100	—	—	—	505
Revere (top) ...	—	19	45·5	80	—	100	—	—	520
Scotch Hill ...	—	12·6	42	—	100	—	—	—	550
Jamison	—	—	21·5	55	—	100	—	—	650
Vogele (bottom)	—	—	—	16	72	—	100	—	915
Vogele (top) ...	—	—	—	16·5	69·5	—	100	—	925
Berkley	—	—	—	11·5	63	—	—	100	980
Seal..............	—	—	—	—	29	43	67†	100	1120
Ocean	—	—	—	—	—	—	—	50	1800
* 7 weeks.						† 9 weeks.			
Wyodak	64	82	100	—	—	—	—	—	140
Hotchkiss	64	91	100	—	—	—	—	—	140
Milk River	56·5	94	100	—	—	—	—	—	150
Colstrip	37	82	100	—	—	—	—	—	225
Wadge	32	85	—	100	—	—	—	—	240
Owl Creek	17	51	77	—	100	—	—	—	332
Gantar	16	51	68·5	—	100	—	—	—	332
King	16·5	50	74·5	100	—	—	—	—	334
Castlegate	19	50	72	88	100	—	—	—	334

(b) *By chemical oxidants.* After a number of chemical oxidising agents had been tried, the most suitable was considered to be a mixture of hydrochloric acid and potassium chlorate (Hoffmeister's reagent). With this reagent a measure of the reactivity of the ulmins can be obtained fairly rapidly. The coals, freed from hydrocarbons and resins as previously described, were ground so as just to pass through a 150-mesh (Tyler U.S. standard) sieve, care being taken to avoid the production of fine dust. Several 0·5-g. samples of each of the treated coals were heated with 50 c.c. of *N*-hydrochloric acid and different weighed amounts of potassium chlorate in stoppered pressure bottles (370 c.c. capacity) in a bath of boiling water, during 6 hours. The bottles were allowed to cool over-night before being opened, and their contents were then filtered and the proportions of insoluble material determined. In recent work, this method has been modified in minor details.

A convenient measure of the reactivity of the coal ulmins, as determined by chemical oxidation, is given by the calculated percentage production of soluble products caused by 0·5 g. of potassium chlorate, such as is recorded in Table I as the "reactivity index." Such determinations may not be as accurate as those given by atmospheric oxidation, but they are more readily obtained, and for that reason we have chosen them for use in our table of "rational analyses." They are sufficiently accurate for practical purposes. This method of measuring the reactivity of the coal ulmins (see Table V) arranges the coals in nearly the same order as do the methods employing atmospheric oxidation, the younger coals, Colstrip, Owl Creek, and Gantar, again proving exceptions to the general relationship between reactivity and carbon content.

Determination of Hydrocarbons and Resins.—For some of the determinations, the usual method of separating the γ_1- and γ_2-compounds (see Cockram and Wheeler, *loc. cit.*) was simplified. The coals were extracted with pyridine in Soxhlet apparatus, in an atmosphere of nitrogen, during 16 hours. The pyridine solution was concentrated to small bulk, excess of chloroform added, and the pyridine neutralised with dilute hydrochloric acid, thus causing precipitation of the insoluble β-compounds and the dispersed γ_3- and γ_4-compounds. The γ_1- and γ_2-compounds, in solution, were estimated by evaporating off the chloroform and weighing.

Determination of Organised Plant Entities.—When the production of soluble ulmins is effected by atmospheric oxidation of the coals (freed from hydrocarbons and resins) at 150°, the determination of the proportion of organised plant entities is straightforward, for they, together with any mineral matter, constitute the residue remaining insoluble in alkaline solutions when the oxidation has

TABLE V.

Chemical Oxidation.

Percentage formation of soluble ulmins.

Name of coal.	Weight of $KClO_3$ used. 0·25.	0·50.	0·75.	1·00.	1·25.	2·50.
Bailey's Mills	31·5	61·5	—	—	—	—
Skillcross	30·0	58·8	—	—	—	—
Elm Grove	29·0	56·7	—	—	—	—
Monongah	—	47·0	65·7	—	—	—
Delmont	—	45·0	67·1	—	—	—
Revere (bottom)	—	42·5	57·9	—	—	—
Greensburg	—	41·5	57·7	—	—	—
Trotter	—	39·6	54·9	—	—	—
Revere (top)	—	—	51·0	61·5	—	—
Martin	—	30·2	50·0	—	—	—
Scotch Hill	—	—	49·0	60·5	—	—
Berkley	—	—	—	—	56·5	—
Jamison	—	—	—	46·1	—	—
Vogele (top)	—	—	—	—	49·0	—
Vogele (bottom)	—	—	—	—	44·3	—
Seal	—	—	—	—	41·5	—
Ocean	—	—	—	—	—	66·0
Wyodak	48·1	80·0	—	—	—	—
Wadge	39·5	71·2	—	—	—	—
Hotchkiss	44·6	70·0	—	—	—	—
Knife River	33·5	70·0	—	—	—	—
Milk River	42·7	68·5	—	—	—	—
Pinnacle	30·0	55·3	—	—	—	—
Owl Creek	30·0	54·3	—	—	—	—
King	30·0	53·2	64·6	—	—	—
Gantar	25·0	52·1	—	—	—	—
Colstrip	—	50·5	—	—	—	—
Castlegate	—	49·0	63·8	—	—	—
Sunnyside	—	48·0	60·7	—	—	—

been carried to completion. This takes several weeks, however, and some more convenient method of estimation is essential. As the result of extensive tests in comparison with the results obtained by atmospheric oxidation, the following procedure, which gives reasonably accurate estimations, was adopted.

A sample (0·5 g.) of the coal (freed from hydrocarbons and resins) was boiled during 7 hours under a reflux condenser with one or other of the solutions specified in the accompanying table, according to its carbon content.

Carbon content of coal (% on ash-free, dry basis).	Oxidising solution. Nitric acid, c.c.	Water, c.c.	$KClO_3$, g.
<79	37·5 (N)	12·5	Nil
79—83	50 (N)	Nil	,,
83—86	30 ($2N$)	20	0·5
86—88	35 ($2N$)	15	0·75
88—89	40 ($2N$)	10	1·0
89—90	50 ($2N$)	Nil	3·0

The ash-free material insoluble in potassium hydroxide solutio after this treatment was estimated to be the resistant plant entitie

with those obtained by atmospheric oxidation of the coals.

This work has been carried out for the Safety in Mines Research Board in co-operation with the United States Bureau of Mines. We wish gratefully to acknowledge, in particular, the help given us by Dr. David White, by the staff of the U.S. Geological Survey and by the analytical staff of the Bureau of Mines Experiment Station at Pittsburgh.

SAFETY IN MINES RESEARCH LABORATORIES,
SHEFFIELD. [*Received, August 21st, 1928.*]

APPENDIX.

TABLE VI.

Coal Analyses.

Coal.	Moisture, %, as received.	Per cent. on dry coal. Volatile matter.	Ash.	Ultimate analysis, %, on ash-free, dry coal. C.	H.	N.	S.
Bailey's Mills* [Barnesville, Ohio]	2·0	43·8	13·5	78·9	5·9	1·3	4·4
Elm Grove [Wheeling, W. Virg.]	2·2	41·4	4·5	81·1	5·3	1·6	3·2
Skillcross, No. 2 [Wheeling, W. Virg.]	3·0	42·4	7·8	81·1	5·6	1·4	4·4
Monongah, No. 63† [Fairmont, Pa.]	1·6	38·0	4·6	83·3	5·6	1·9	0·6
Irwin Strip [Delmont, Pa.]	1·0	38·5	5·4	84·5	6·0	1·8	2·4
Martin [Fairchance, Pa.]	0·4	39·1	5·6	84·8	5·6	*ca.*1·5	0·9
Revere† [Uniontown, Pa.]	3·5	31·6	6·7	85·2	5·5	1·9	0·8
Scotch Hill [Newburg, W. Virg.]	1·2	34·2	3·6	85·2	5·2	1·3	1·0
Revere* [Uniontown, Pa.]	3·6	30·6	5·9	86·1	5·4	1·8	0·7
Jamison, No. 20 [Pleasant Unity, Pa.]	0·5	31·8	5·6	86·5	5·6	*ca.*1·5	0·8
Vogele† [Ligonier, Pa.]	2·9	24·5	12·7	86·6	5·2	1·9	2·5
Greensburg, No. 2 [Greensburg, Pa.]	0·8	33·7	3·0	86·7	5·5	*ca.*1·5	0·9
Vogele* [Ligonier, Pa.]	3·6	24·8	14·3	87·4	5·4	1·9	1·8
Trotter [Connellsville, Pa.]	0·6	30·9	6·0	87·6	5·7	*ca.*1·5	0·8
Berkley [Meyersdale, Pa.]	3·7	20·6	10·3	87·6	5·0	1·9	1·7
Ocean† [Midland, Maryland]	0·8	17·5	6·3	89·0	4·7	1·9	0·9
Seal† [Meyersdale, Pa.]	2·7	21·6	7·8	89·1	5·1	2·1	1·0

* Bottom part of seam. † Top part of seam.

TABLE VI (*contd.*).

Coal.	Moisture, %, as received.	Per cent. on dry coal. Volatile matter.	Ash.	Ultimate analysis, %, on ash-free, dry coal. C.	H.	N.	S.
Wyodak [Gillette, Wyoming]	31·1	43·7	7·7	71·9	5·4	1·2	0·6
Knife River [Beulah, N. Dakota]	35·0	41·9	7·0	72·9	4·9	1·1	1·1
Milk River [Chinook, Montana]	26·4	38·2	9·6	73·4	5·4	1·7	0·7
Hotchkiss [Sheridan, Wyoming]	22·2	42·7	5·6	73·4	6·0	1·3	0·6
Colstrip [Colstrip, Montana]	25·8	39·8	8·0	74·6	5·3	1·2	0·9
Owl Creek [Gebo, Wyoming]	12·9	39·6	6·6	77·0	5·7	1·7	0·6
Wadge [Routt Co., Colorado]	9·9	40·4	5·2	78·4	5·1	1·9	1·2
Gantar [Roundup, Montana]	15·0	36·3	5·4	78·4	5·3	1·4	0·5
Pinnacle [Routt Co., Colorado]	9·2	39·5	2·9	79·1	5·7	1·8	0·6
King, No. 1 [Hiawatha, Utah]	5·7	43·9	4·9	80·7	5·8	1·5	0·9
Castlegate, No. 2 [Castlegate, Utah]	3·7	40·9	5·6	81·5	5·5	1·3	0·3
Sunnyside, No. 1 [Sunnyside, Utah]	3·8	40·3	2·8	82·5	5·8	1·8	1·0

CCCXCI.—*The Addition of Halogens to Unsaturated Acids and Esters. Part II. The Addition of "Bromine Chloride" to Phenylpropiolic Acid.*

By NORMAN WILLIAM HANSON and THOMAS CAMPBELL JAMES.

IT has been shown in Part I (this vol., p. 1955) that an equimolecular mixture of bromine and chlorine, dissolved in carbon tetrachloride ("bromine chloride" solution), reacts additively with cinnamic acid to form the two externally compensated stereoisomerides corresponding to the formula C_6H_5·CHCl·CHBr·CO_2H.

Similar experiments with phenylpropiolic acid in the place of cinnamic acid have now given a mixture from which, by fractional crystallisation from light petroleum, two, and only two *acids* have been isolated. These are the geometrical isomerides which theory demands from the structural formula C_6H_5·CCl:CBr·CO_2H.

By exposure of a chloroform solution of the higher-melting acid (129°), mixed with a little bromine, to direct sunlight, this acid was almost entirely converted into its lower-melting isom[illegible]
[illegible]

cinnamic acids, since, under similar conditions, the higher-melting (m. p. 139°) αβ-dibromocinnamic acid is partly transformed into its lower-melting (m. p. 100°) isomeride (Roser and Haselhoff, *Annalen* 1888, **247**, 140), and the lower-melting (m. p. 101°) αβ-dichlorocinnamic acid undergoes isomerisation into the higher-melting (m. p. 121°) acid (Stoermer and Heymann, *Ber.*, 1913, **46**, 1349) The stable transformation products in both of these cases possessed the *cis*-configuration, as will be shown.

The interconvertibility of the β-chloro-α-bromocinnamic acids is indicative of their geometrically, and not structurally isomeric relationship; thus the addition of " bromine chloride " corresponds to that of bromine to phenylpropiolic acid in non-hydroxylic solvents, since in this case also a mixture of the two geometrically isomeric αβ-dibromocinnamic acids is formed (Roser and Haselhoff, *loc. cit.*).

The corresponding addition of chlorine, however, gives rise to only one product, namely, *cis*-αβ-dichlorocinnamic acid (m. p. 121°) (Nissen, *Ber.*, 1892, **25**, 2665), but this apparent anomaly can probably be explained by the extremely labile nature of the lower-melting (100°) *trans*-isomeride (Stoermer and Heymann, *loc. cit.*).

The positions occupied by the respective halogen atoms in the chlorobromocinnamic acids have been determined by a study of the chlorobromoindone which is produced when the lower-melting (112°) isomeride is treated with cold concentrated sulphuric acid; this reaction, moreover, establishes the *cis*-configuration of this acid. The higher-melting acid is therefore the *trans*-isomeride, and this conclusion is borne out by the fact that it is not affected by treatment with sulphuric acid.

Indeed, it has been found most convenient to prepare the chlorobromoindone directly from the product of the interaction of phenylpropiolic acid and " bromine chloride," since the indone was readily separable from the residual *trans*-acid by solution in hot light petroleum.

Although this indone has the same melting point (105°) as that of the compound shown by Roser and Haselhoff (*Annalen*, 1888, **247**, 148) to be 2-chloro-3-bromo-1-ketoindene, yet an examination of its reactions has led to the conclusion that it is isomeric with the latter, and possesses the structure designated by 3-*chloro*-2-*bromo*-1-*ketoindene*. The evidence adduced for such a structure is based on the fact, definitely established by Schlossberg (*Ber.*, 1900, **33**, 2425), that the halogen atom which occupies the α-position to the phenylene group (*i.e.*, the 3-position) is the more readily replaceable by univalent atoms or radicals.

The chlorobromoindone obtained from *cis*-chlorobromocinnamic

acid condensed readily with aniline, to form an anilido-derivative identical with that obtained by Roser and Haselhoff (*loc. cit.*) from 2 : 3-dibromoindone, which was therefore 2-bromo-3-anilidoindone.

The fact that as a result of this condensation hydrogen chloride is eliminated (as a quantitative experiment proved) establishes the structure of the substance as 3-chloro-2-bromoindone. Additional evidence favouring such a structure is afforded by the fact that the analogous piperidyl derivative was identical with that prepared by Roser and Haselhoff from 2 : 3-dibromoindone and piperidine.

Furthermore, an authentic specimen of 2-chloro-3-bromoindone, prepared by boiling 2 : 3-dichloroindone with alcoholic potassium bromide (Roser and Haselhoff) proved to be non-identical with the new chlorobromoindone, as was evinced by a mixed melting point, and by the non-identity of their *oximes*.

Consequently, the new indone must be formed by the elimination of water from *cis*-β-chloro-α-bromo-β-phenylacrylic acid, m. p. 112°, and since this is directly obtainable from its isomeride, m. p. 129°, *the latter must possess the trans-configuration.* The following table summarises the physical properties of these new chlorobromocinnamic acids and the already known αβ-dihalogenocinnamic acids :

Cinnamic acid.		M. p.	Crystalline form.	Solubility.	Stability.
β-Chloro-α-bromo-	*cis*	112°	Needles	More sol.	Stable
	trans	129	Plates	Less ,,	Labile
αβ-Dibromo-	*cis*	100	Needles	More ,,	Stable
	trans	139	Plates	Less ,,	Labile
αβ-Dichloro-	*cis*	121	Plates	Less ,,	Stable
	trans	100	Rhombic tablets	More ,,	Labile

The new chlorobromocinnamic acids are seen to possess physical properties analogous in every respect with those of their dibromo-congeners.

The positions taken up by the constituent atoms of the " bromine chloride " molecule when this unites with phenylpropiolic acid—the more negative atom uniting with the β-carbon atom—are the same as in the case where cinnamic is substituted for phenylpropiolic acid.

By a series of experiments conducted as described in Part I, " bromine chloride " has been found to react with phenylpropiolic acid at a much more rapid rate than either bromine or chlorine alone, the reaction being of the bimolecular type, without an inhibition period. Thus in yet another way is the reaction parallel to that for cinnamic acid and " bromine chloride."

cinnamic acids above described (the *trans*-isomerides were no employed owing to their ready transformation into the *cis*-acids) i interesting.

The nature and extent of these reactions were determined by series of experiments conducted as already described by William and James (this vol., p. 344). The mixed solutions of acid an halogen were sealed up in colourless glass bulbs and exposed t dull light, the residual halogen after definite time-intervals bein determined by breaking the bulbs under potassium iodide an titrating the liberated iodine with standard thiosulphate.

The results obtained with bromine showed that in all three case the amount of this halogen which disappeared was extremely smal even after several weeks, and may even then have been due t substitution in the phenyl radical, so that no bromine additio products could be prepared.

αβ-Dichlorocinnamic acid formed an addition product wit chlorine, *viz.*, *ααββ-tetrachloro-β-phenylpropionic acid*, m. p. 130° This is the one product expected on theoretical grounds; it contain *no* asymmetric carbon atoms and is therefore not potentiall optically active.

The results for αβ-dibromocinnamic acid and chlorine indicate that some replacement of the bromine in the acid by chlorin occurred, but no recognisable product could be isolated and ther was no further reaction when the concentration of the total haloge was approximately half its initial value. This attainment of a approximate "equilibrium" may be ascribed either to the form ation of an actual equilibrium between original acid, replaced acid chlorine and bromine, or to the total disappearance of the chlorin by its substitutive and additive reactions, in which case the residua halogen would be the bromine liberated by replacement, whic would be practically inert towards these acids.

A similar partial replacement of bromine by chlorine, and attain ment of an approximate "equilibrium," occurred in the reactio between β-chloro-α-bromocinnamic acid and chlorine, but in thi case about five-sixths of the halogen had disappeared at that stage The main product of this reaction was the dichloride of the chloro bromo-acid, *viz.*, *αββ-trichloro-α-bromo-β-phenylpropionic acid*, m. p 127°, but a small quantity of ααββ-tetrachloro-β-phenylpropioni acid was also formed.

The former of these products is the only addition compoun expected on theoretical grounds: it contains only one asymmetri to ...bon atom, and may therefore be resolvable.

replac...responding experiments with "bromine chloride" in place o The ch... halogens indicated that it did not react as a molecule o

uch in these cases, the chlorine portion only appearing to be eactive.

The properties of the dichloro- and chlorobromo-cinnamic acids of forming addition products with chlorine but not with bromine, and of the replacement of part of the bromine by chlorine in the case of the latter acid, are not unique. For instance, tetraphenylethylene forms no addition product with bromine (Behr, *Ber.*, 1870, **3**, 753) but yields with chlorine a dichloride (Norris, Thomas, and Brown, *Ber.*, 1910, **43**, 2940). Further it has recently been hown by Meisenheimer (*Annalen*, 1927, **456**, 142) that triphenylbromoethylene, althongh it does not unite with bromine, reacts with excess of chlorine with replacement of the hromine atom and ormation of a dichloride of the resulting product, triphenyltrichloroethane.

EXPERIMENTAL.

When a suspension of phenylpropiolic acid in carbon tetrachloride was treated at 0° and in the dark with " bromine chloride " (1 mol.) dissolved in the same solvent, the acid gradually went into solution. After a few hours the solvent was removed by evaporation in a vacuum, and the resulting crystalline mass dissolved in hot chloroform. On adding light petroleum to this solution until cloudy and allowing it to cool, colourless crystalline plates and clusters of straw-coloured needles were deposited. The mother-liquid was decanted, and the mixture of crystals warmed with light petroleum; the needles alone went into solution. The plates, after being washed with more hot light petroleum, melted at 129° (Found: Br, 30·0; Cl, 13·8. $C_9H_6O_2ClBr$ requires Br, 30·6; Cl, 13·6%). The hot petroleum from the first extraction deposited, on cooling, clusters of long, straw-coloured needles, m. p. 112° (Found: Br, 30·0; Cl, 13·7%). The proportion of the higher- to the lower-melting *chlorobromocinnamic acid* was approximately 1 : 4. A successful separation of the two acids could not be accomplished by any of the other methods commonly employed in similar cases.

When the mixed chlorobromocinnamic acids obtained by addition of " bromine chloride " to phenylpropiolic acid were rubbed with excess of cold concentrated snlphuric acid, a dark brown solution was formed, which, when poured into a large volume of cold water, yielded a quantity of golden-yellow flocks. Hot light petroleum dissolved the coloured constituent of the dried product, leaving undissolved a small proportion (about one-fifth of the original mixture) of small colourless plates of the higher-melting chlorobromocinnamic acid (m. p. 129°). The petroleum extract deposited

m. p. 105° (Found: Br, 32·7; Cl, 10·9. C_9H_4OClBr requires B 32·9; Cl, 10·8%).

The indone, when warmed with excess of aniline in alcohol solution, yielded bright scarlet needles of 2-bromo-3-anilidoindon m. p. 170°, as described by Roser and Haselhoff (*loc. cit.*). Th hydrogen chloride was eliminated by this condensation is prove by the following results:

0·204 G. of the indone was treated with alcoholic aniline, and t anilido-compound removed. The filtrate gave 0·1220 g. of silv halide, which was not reduced in weight when warmed in a strea of chlorine, and was hence silver chloride (Calc. for 100% evolutio of hydrogen chloride: AgCl, 0·1200 g.).

The chlorobromoindone, when treated with piperidine as f aniline, gave bright red tables of 3-piperidyl-2-bromo-1-ketoinden m. p. 117° (decomp.) (Roser and Haselhoff, *loc. cit.*).

By boiling the indone in alcoholic solution with hydroxylami hydrochloride, pouring the mixture into water, and crystallising t precipitated yellow powder from alcohol, *3-chloro-2-bromo-1-ket indene oxime* was obtained as silky yellow needles, m. p. 19 (decomp.) (Found: Br, 30·1; Cl, 14·1. $C_9H_5ONClBr$ requir Br, 30·9; Cl, 13·7%).

2-Chloro-3-bromo-1-ketoindene, prepared as described by Rose and Haselhoff, melted at 105°; a mixture of this and the above described 3-chloro-2-bromo-1-ketoindene melted indefinitely a 65—100°. The *oxime* of the former compound, prepared as describe for the latter, melted at 184° (decomp.) (Found: Br, 30·3; Cl, 13·6%

The results of kinetic experiments with phenylpropiolic acid an "bromine chloride," bromine, and chlorine, respectively, are sum marised in the table. The corresponding figures for cinnamic ac and these reagents are given for comparison purposes. Experimen were conducted at 0°, in the dark, and in carbon tetrachlorid solution. The bimolecular velocity coefficient $k = 1/t \cdot x/a(a - x$ is calculated on the basis of t in hours and concentrations (a and in g.-mols. per litre.

Acid.	Reagent.	Limits of k.	Mean k.
Phenylpropiolic	Bromine chloride	4·43—3·76	4·11
	Bromine	0·0733—0·0680	0·0700
	Chlorine	0·0540—0·0344	0·0420
Cinnamic	Bromine chloride	133—96·3	104
	Bromine	0·173—0·041	0·146
	Chlorine	0·265—0·153	0·209

Although phenylpropiolic acid is more unsaturated than cinnami acid, the halogens react with the former at a slower rate than wit the latter. The hydrogen atoms in the cinnamic acid side chai probably play an important part in this connexio

cis-αβ-Dichlorocinnamic acid, treated with chlorine (1 mol.) in rbon tetrachloride solution, and exposed to diffused light for weeks, yielded a product which crystallised from carbon tetraloride in colourless prisms, m. p. 130° (Found: Cl, 48·8. $H_6O_2Cl_4$ requires Cl, 49·2%). The product is therefore αα*ββ-tetraloro-β-phenylpropionic acid*.

cis-β-Chloro-α-bromocinnamic acid reacted with chlorine, with rtial replacement of bromine by chlorine, and formation of the rresponding addition product, ααββ-tetrachloro-β-phenylpropionic id in small amount, the main product being the dichloride of the iginal chlorobromo-acid, *viz.*, αββ-*trichloro-α-bromo-β-phenylpro-onic acid*, m. p. 127° (Found: Br, 24·0; Cl, 31·7. $C_9H_6O_2Cl_3Br$ quires Br, 24·0; Cl, 32·0%). The products were separated by ctional crystallisation from carbon tetrachloride.

One of us (N. W. H.) desires to record his indebtedness to the partment of Scientific and Industrial Research for a maintenance ant.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
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ABERYSTWYTH. [*Received, August 24th*, 1928.]

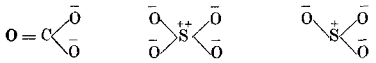
CCXCII.—*Studies in Complex Salts. Part I. The Preparation and Properties of Some Selenitopentamminecobalt Salts.*

By HARRY LISTER RILEY.

LTHOUGH carbonatopentammine compounds have been described Verner and Goslings, *Ber.*, 1903, **36**, 2378), the carbonate ion pears to have a greater tendency to occupy two positions in the mplex, as judged from a consideration of methods of preparation d relative yields. Complex salts have been described containing lphato-, sulphito- (Riesenfeld, *Z. anorg. Chem.*, 1924, **132**, 99), romato- (Briggs, J., 1919, **115**, 67), and selenato- (Meyer, *Z. anorg. hem.*, 1921, **118**, 1) groups, and in the case of the first three groups oth pentammine and tetrammine compounds have been prepared. iesenfeld pointed out (*loc. cit.*) that the sulphito-group almost variably occupies only one position in the co-ordination complex, d advanced experimental evidence in favour of a tetrahedral ructure for those compounds where this group has been represented occupying two positions in the complex. The tetrammine lphato- and chromato-compounds were prepared from the corresonding carbonato- or diaquo-tetrammine compound, and there is

no record of these compounds having been prepared in a manner similar to that employed in the case of the carbonatotetrammine compound (Jörgensen, *Z. anorg. Chem.*, 1892, **2**, 282).

The reason for this difference in the properties of these ions becomes apparent on the basis of modern electronic theory. The tendency of a molecule or ion to enter the co-ordinated complex depends on its possession of a "lone pair" of electrons and upon the distribution of the charges within the molecule or ion. A comparison of the structure of the various ions under consideration at once suggests an explanation of their differences in behaviour.



Carbonato-. Co-ordinate valency usually 2.
Sulphato-. Sulphito-. Co-ordinate valencies usually 1.

The effect of the positive charges on the sulphur atom is to cause the electrons round the oxygen atoms to be held much more firmly and to reduce their tendency to form a co-ordinate link. When one link is formed, the tendency to form a second will be less still. In the carbonato-ion the carbon atom is electrically neutral, so the negative oxygen atoms will possess a greater tendency to form a co-ordinate link than if the carbon atom were positively charged. The formation of one co-ordinate link will reduce the tendency to form a second.

In order to test the above ideas, it was decided to attempt the preparation of some selenito-complex salts (which have not previously been described) by a method similar to that employed in the preparation of carbonato-tetrammine and -pentammine compounds, examining the product of oxidation for both pentammine and tetrammine compounds.

EXPERIMENTAL.

Preparation of Selenitopentamminecobaltic Chloride.—To 18 g. of freshly precipitated cobaltous hydroxide were added 22 g. of selenium dioxide (prepared from metallic selenium by oxidation with nitric acid and subsequent sublimation), and 11 g. of ammonium chloride, followed by a little water and a large excess of ammonia (d 0·880). The whole was well stirred until everything soluble had dissolved. A rapid current of air was passed through the filtered solution until it no longer contained free ammonia (about 12 hrs.), its colour changing from brownish-red to a deep ruby-red. The solution (about 400 c.c.) was evaporated to 100 c.c. in a vacuum over concentrated sulphuric acid. As no crystallisation had occurred

at this stage, 250 c.c. of alcohol were slowly added with continuous stirring. A deep red, oily liquid separated which slowly solidified to a crystalline mass. The clear supernatant liquid was decanted, and on being tested with barium chloride showed the presence of selenite ions. The solid mass was dissolved in 100 c.c. of water and again precipitated with 250 c.c. of alcohol. The supernatant liquid, which was again decanted, gave no precipitate with barium chloride. The solid was dissolved in 80 c.c. of water, 150 c.c. of alcohol were added, and the mixture was kept for 2 days, a few c.c. of alcohol being added from time to time. It was thus possible to grow quite large crystals, some of them about 2 cm. long, which on examination under the microscope, proved to be not single crystals but aggregates of small crystals belonging to either the rhombic or the tetragonal system. The large crystals were deep brownish-red, whereas the small, rapidly precipitated crystals were much lighter in colour. A yield of over 80% of *selenitopentamminecobaltic chloride* (of above 98% purity) was obtained (Found: Co, 19·36; SeO_3, 40·81; NH_3, 27·34; Cl, 11·72; Co : SeO_3 : NH_3 : Cl = 1·02 : 1·00 : 5·01 : 1·03. $[Co(SeO_3)(NH_3)_5]Cl$ requires Co, 19·22; SeO_3, 41·49; NH_3, 27·72; Cl, 11·57%). Some of the crystals, after being air-dried, were placed in a vacuum desiccator over sulphuric acid for 2 days. No loss in weight occurred.

Analysis.—The following method was adopted for the analysis of the crystals. *Selenium.* About 0·3 g. of the substance was dissolved in 100 c.c. of water, 2—3 c.c. of concentrated hydrochloric acid were added, and then 30 c.c. of saturated sulphurous acid solution, and the whole was boiled for 5 hours, with the addition of more sulphurous acid from time to time. The precipitated selenium was washed, dried at 90—95°, and weighed.

Cobalt. The filtrate from the selenium was evaporated to dryness with the addition of a slight excess of sulphuric acid. The cobalt sulphate formed was heated at 400—450° and weighed. Ammonia and chlorine were estimated by the usual methods.

The reactions of the compound proved conclusively that it possessed the assigned constitution. Its solution in water, in which it is extremely soluble, gives no precipitate with barium chloride in the cold, showing the absence of selenite ions. On boiling, a precipitate containing barium, cobalt, and selenium is thrown down. Sulphur dioxide precipitates selenium from a hot solution containing hydrochloric acid, but the precipitation is complete only after prolonged boiling (see analysis, above). A concentrated solution of the salt containing a little sulphuric acid gives a precipitate with ferrous sulphate solution only after a few minutes' boiling. Hydrogen sulphide gives an immediate precipitate of sulphur and selenium.

Silver nitrate precipitates the chlorine completely from a col solution. Sodium hydroxide only precipitates the cobalt on boiling ammonia being evolved. When a solution of the compound i boiled with dilute hydrochloric acid (1 : 3), a ruby-red, crystallin substance is precipitated; this was shown to be chloropentammine cobaltic chloride : $[Co(SeO_3)(NH_3)_5]Cl + 2HCl = [CoCl(NH_3)_5]Cl_2 + H_2SeO_3$. Molecular-weight determinations (cryoscopic in water indicated that the compound is a binary electrolyte of the abov formula, dissociating to the extent of 80% in 0·23*N*-solution an 97% in 0·1*N*-solution.

Another series of experiments was made in which various fraction obtained by precipitating the original oxidised solution with alcohol were analysed: in no case was the ratio $NH_3 : SeO_3$ less than 5 : 1 The high solubility of these selenito-compounds makes it impossibl to be sure that no tetrammine compound is formed, but the abov experiments prove that, if it is formed at all, it can only be presen in very small amounts.

Selenitopentamminecobaltic Selenite.—An attempt to prepare thi compound was made by the following method: To 18 g. of freshl precipitated cobaltous selenite were added 6 g. of selenium dioxide a little water, and a large excess of ammonia (*d* 0·880). The result ing clear solution was oxidised by a rapid current of air until fre from excess of ammonia (12 hrs.). The solution was evaporated i a vacuum over concentrated sulphuric acid. No crystallisatio occurred, but a thick, oily syrup resulted. This was dissolved in a little water, and the filtered solution precipitated with alcohol, th process being carried out five times. The resulting syrup wa evaporated in a vacuum over concentrated sulphuric acid fo several days, and then solidified to a dark red, crystalline mas [Found: Co, 16·51; SeO_3, 52·75; NH_3, 23·28; H_2O (by diff.), 7·46 $[Co(SeO_3)(NH_3)_5]_2SeO_3,3H_2O$ *requires* Co, 16·29; SeO_3, 52·74 NH_3, 23·50; H_2O, 7·46%], which was extremely deliquescent rapidly changing to a viscous liquid on exposure to the atmosphere The aqueous solution rapidly became turbid. Barium chlorid precipitated barium selenite along with some cobalt selenite from th cold solution. On removing this precipitate and reducing th acidified filtrate with hydroxylamine hydrochloride, selenium wa precipitated, thus indicating the presence of both ionised an co-ordinated selenite groups. Water was shown to be present i the compound qualitatively; it was not removed by long exposur to sulphuric acid in a vacuum. The compound analysed wa probably appreciably decomposed.

An attempt to estimate ionised and co-ordinated selenium separately led to inconclusive results. Hydrolysis always occurre

during attempts to dissolve the substance even in ice-cold water. The analysis showed, however, that the substance does contain the selenito-group in the complex and that the ratio $NH_3 : SeO_3$ is 5 : 1·5, which is in agreement with the proposed formula. The high solubility and rather unstable nature of the substance make it impossible to obtain it pure.

Summary.

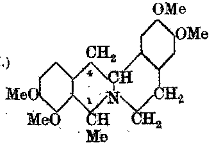
Ions which possess an electrovalency of two show varying co-ordination valencies. The carbonate ion usually occupies two positions, but sometimes only one. Ions of the sulphate and sulphite types possess a greater tendency to occupy one position in the complex. An explanation of this behaviour is advanced, and evidence in agreement with this explanation is obtained from a study of the properties of two selenitopentamminecobaltic salts which were specially prepared for this purpose.

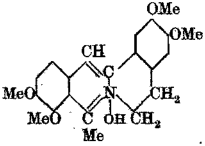
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, July 17th*, 1928.]

CCCXCIII.—*Synthesis of Oxydehydrocorydaline.*

By JOSEPH BLAKE KOEPFLI and WILLIAM HENRY PERKIN, jun.

CORYDALINE, $C_{22}H_{27}O_4N$, the principal alkaloid occurring in *Corydalis cava* and *Corydalis tuberosa*, was first isolated by Wackenroder (*Berz. Jahr.*, 1826, 7, 220); it melts at 133° and has $[\alpha]_D^{20°} + 300°$ (in chloroform). Our knowledge of the constitution of this alkaloid is very largely due to the researches of Dobbie and Lauder (J., 1902, 81, 148), who, mainly as the result of the study of the substances obtained on oxidation and the comparison of these with the corresponding substances derived from berberine under like conditions, concluded that the constitution (I) must be assigned to corydaline.

(I.)




(II.)

This formula represents corydaline as the methyl derivative of tetrahydropalmatine containing the methyl group in the position 1.

This view of the constitution of the alkaloid held the field for

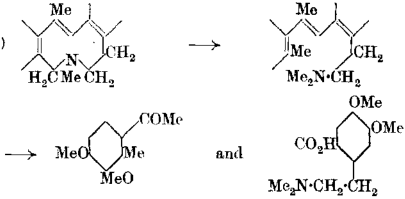
several years and was also adopted by Gadamer (*Arch. Pharm.*, 1910, **248**, 205) after the careful consideration of several alternative expressions. Perhaps the most characteristic property of corydaline is its conversion by mild oxidising agents with loss of four atoms of hydrogen into the yellow base dehydrocorydaline, $C_{22}H_{25}O_5N$, which closely resembles berberine in appearance and in several of its properties and was therefore assumed to be the methylpalmatine (II) containing the methyl group again in position 1. Confirmation of this view was thought to be disclosed by the fact that, for a long time, it was not found possible to convert dehydrocorydaline chloride into derivatives corresponding with oxyberberine and dihydroberberine, and the failure to undergo this characteristic reaction was assumed to be due to the presence of the methyl group in the position 1.

However, in 1922, Gadamer and von Bruchhausen (*Arch. Pharm.*, **259**, 249) succeeded in bringing about this change by treating dehydrocorydaline acetate with sodium hydroxide, and this important result was the first clear indication that the methyl group in corydaline could not be situated in position 1. Further evidence on this point was also furnished by Späth and Lang (*Ber.*, 1921, **54**, 3074), who converted palmatine iodide, by the action of magnesium methyl iodide and subsequent reduction, into two isomeric methyltetrahydropalmatines, neither of which was identical with *dl*-corydaline. Since, however, the researches of Freund and Beck (*Ber.*, 1904, **37**, 4674) have shown that, when the Grignard reagent reacts with salts of berberine, it is the hydrogen atom (1) which becomes replaced, and it may be assumed that the salts of palmatine will behave in a similar manner, the methyltetrahydropalmatines obtained by Späth and Lang should both contain the methyl group in position 1 and one of them should be identical with *dl*-corydaline (I), which, however, is not the case. More conclusive evidence in support of this view and indicating that position 4 must be assigned to the methyl group was subsequently brought forward by von Bruchhausen (*Arch. Pharm.*, 1923, **261**, 31).

This author achieved a partial synthesis of *d*-corydaline by methylating palmatine acetone with methyl iodide and reducing the methylated product with zinc and sulphuric acid. Since the researches of Freund and Speyer (*Annalen*, 1913, **397**, 1) and Freund and Fleischer (*ibid.*, 1915, **409**, 194) have shown that, when substances of the dihydroberberine type, to which palmatine acetone is supposed to belong, interact with methyl iodide, it is the hydrogen atom in position 4 which is reactive and becomes replaced by methyl, von Bruchhausen maintains that his synthesis is strong evidence that, in corydaline, the methyl group must occupy the position 4.

More recently still, von Bruchhausen and Stippler (*Arch. Pharm.*, 927, **265**, 152) converted corydaline methochloride into the ınhydro-base (III) [compare anhydromethyltetrahydropalmatine A), J., 1927, 2262], reduced the methosulphate of this with sodium ımalgam to (IV), and showed that this substance on oxidation with ›ermanganate yields methylacetoveratrone and, with ozone, ł : 5-dimethoxy-2-dimethylaminoethylbenzoic acid. Not only is ·his interesting series of decompositions (compare J., 1916, **109**, ꞔ21), which may be represented by the partial formulæ

(III.)

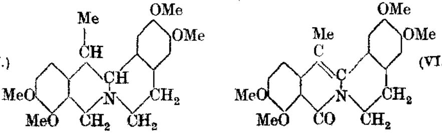


(IV.)

aluable general evidence of the constitution of corydaliue, but, in ›articular, the formation of methylacetoveratrone may be taken as upporting the view that the methyl group in corydaline occupies the osition 4.

This brief sketch shows that the evidence which gradually accu- ıulated had become strongly in favour of the view that the consti- ıtion of corydaline must be represented by (V) and not by the

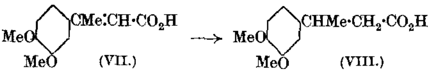
(V.)



(VI.)

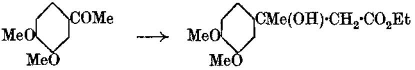
›rmula (I) of Dobbie and Lauder but, in order definitely to settle ıis matter, it seemed to us that it would be of interest to attempt › carry out a complete synthesis either of corydaline itself or of ›me highly characteristic derivative of the alkaloid. The derivative ·lected in the first place was oxydehydrocorydaline (VI), and the ꞔperience gained in the course of previous synthetical work in this ꞔoup of alkaloids suggested that the best starting point for this

to obtain by reducing the corresponding β-*veratrylcrotonic acid* (VII). But the acid (VII) proved difficult to prepare : among the unsuccessful attempts to obtain it may be mentioned the condensation of

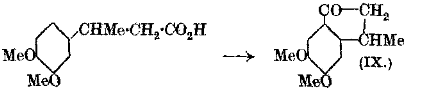


acetoveratrone with malonic acid and acetic anhydride (Massot, *Ber.*, 1894, **27**, 1225) or acetic anhydride and sulphuric acid (Meldrum, J., 1908, **93**, 598), and various processes involving the Claisen condensation.

Ultimately, acetoveratrone was found to interact readily with ethyl bromoacetate in the presence of zinc (Lindenbaum, *Ber.*, 1917, **50**, 1270) :



the crude ethyl β-veratryl-β-hydroxybutyrate, when distilled under reduced pressure, decomposed with the loss of water and formation of *ethyl* β-*veratrylcrotonate*. The free acid (VII), readily obtained from the ester by hydrolysis, was reduced by sodium amalgam to β-*veratrylbutyric acid* (VIII) and this, on treatment with sulphuric acid, yielded 5 : 6-*dimethoxy*-3-*methyl*-1-*hydrindone* (IX), a substance

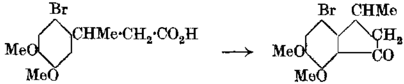


which was carefully characterised by conversion into the *oxime* and iso*nitroso*-derivative.

The formation of the hydrindone (IX) as the sole product of the dehydration is due to the well-known tendency to ring closure in the 6-position, para to one of the methoxy-groups. As it was necessary for the purpose of the synthesis of oxydehydrocorydaline that this should not occur but that the hydrindone formation should take place in the position 2, the 6-position was protected by the introduction of a bromine atom (Haworth, Perkin, and Stevens, J., 1926, 1764; Haworth, Koepfli, and Perkin, J., 1927, 548). 6-*Bromo*-β-*veratrylbutyric acid* (X), obtained by treating the acid (VIII) in glacial acetic acid solution with bromine, readily [illegible]

ıng closure when warmed with sulphuric acid and yielded 4-*bromo-* : 7-*dimethoxy*-3-*methyl*-1-*hydrindone* (XI).

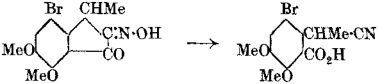
X.)



(XI.)

When the *isonitroso*-derivative (XII) of this hydrindone, dis- ɔlved in sodium hydroxide, was treated with toluene-*p*-sulphonyl hloride, it underwent the Beckmann transformation and a good ield of 6-bromo-2-carboxy-3 : 4-dimethoxy-α-phenylpropionitrile XIII) was obtained.

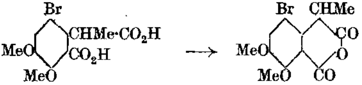
XII.)



(XIII.)

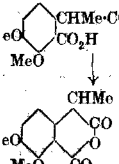
This was converted, on hydrolysis, into 6-bromo-3 : 4-dimethoxy- -methylhomophthalic acid (XIV), a gum from which the crystalline *ıhydride* (XV) was obtained by the action of acetyl chloride.

XIV.)



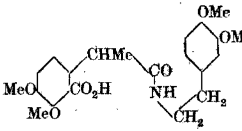
(XV.)

he anhydride was hydrolysed in alkaline solution and debrominated ith sodium amalgam, and the crude 3 : 4-dimethoxy-α-methyl- ɔmophthalic acid (XVI) converted into the *anhydride* (XVII) by ıe action of acetyl chloride.



(XVI.)

(XVII.)

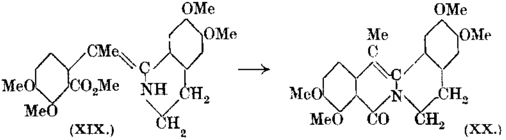


(XVIII.)

he anhydride (XVII) was now combined with β-veratrylethylamine Iaworth, Perkin, and Pink, J., 1925, **127**, 1709) by boiling the two ıbstances together in benzene solution, the *N*-β-veratrylethyl- : 4-dimethoxy-α-methylhomophthalamic acid (XVIII) obtained ıs converted *into the methyl ester, and this treated with phos-*

phorus oxychloride in the expectation that methyl alcohol as well as water would be eliminated with the formation of oxydehydrocorydaline just as, for example, the methyl ester of *N*-β-veratrylethyl-3 : 4-dimethoxyhomophthalamic acid passes so easily under the same conditions directly into oxypalmatine (Haworth, Koepfli, and Perkin, J., 1927, 549).

However, in the present instance, the methyl ester lost only water on treatment with phosphorus oxychloride and yielded a substance, $C_{23}H_{27}O_6N$, which was clearly *6 : 7 : 3′ : 4′-tetramethoxy-9-methyl-2′-carbomethoxy-3 : 4-dihydroprotopapaverine* (XIX),* because when heated at 150—170° it yielded oxydehydrocorydaline (XX) with elimination of methyl alcohol.



(XIX.) (XX.)

It has already been pointed out (p. 2990) that oxydehydrocorydaline was first prepared by Gadamer and von Bruchhausen from dehydrocorydaline acetate by the action of sodium hydroxide, and these investigators describe it as crystallising from acetic acid in pale yellow, four-sided tablets, m. p. 228—228·5°. The substance which we obtained synthetically, after repeated crystallisation from alcohol, was nearly colourless and melted at 235—236°. We are much indebted to Dr. von Bruchhausen for kindly sending us a specimen of the oxydehydrocorydaline obtained from dehydrocorydaline acetate. After two crystallisations from alcohol, this was still pale yellow but the m. p. had risen to 234—236°, and a mixture with the synthetical substance showed no depression in melting point. There can therefore be no doubt that the two specimens are identical and that the substance obtained synthetically is in fact oxydehydrocorydaline. This synthesis of the substance clearly demonstrates that the constitution of corydaline must be that represented by formula (V).

Preliminary experiments made with the object of converting oxydehydrocorydaline into *dl*-corydaline by electrolytic reduction seem to indicate that this process does not take place so readily as the conversion of oxyberberine into tetrahydroberberine (Perkin, J., 1918, **113**, 737). When larger amounts of material are available it will be possible to decide whether the change can be brought about

* For nomenclature, see Buck, Perkin, and Stevens (J., 1925, 127, 1462).

n this way or whether some other process of reduction must be employed.

EXPERIMENTAL.

Acetoveratrone, $C_6H_3(OMe)_2{\cdot}COMe$.—Veratrole (290 g.), prepared by the action of methyl sulphate on guaiacol (Perkin and Weizmann, T., 1906, **89**, 1649), was dissolved in carbon disulphide (750 c.c.) and mixed with acetyl chloride (197 g.). Aluminium chloride (290 g.) was added to the ice-cold mixture in small portions with constant shaking, and the reaction completed by warming at 50° for a short time. The magenta-coloured crystalline mass was separated from the carbon disulphide and decomposed with ice, the whole extracted with chloroform, and the chloroform solution washed with dilute sodium hydroxide solution and with water and dried over calcium chloride. After removal of the solvent on the steam-bath, the residue was distilled under reduced pressure, acetoveratrone being obtained as a colourless oil (297 g.), b. p. 160—162°/10 mm., which crystallised on standing.

Ethyl β-Veratrylcrotonate (formula as VII).—Acetoveratrone (45 g.) and ethyl bromoacetate (50 g.) in dry benzene (280 c.c.) were placed in a 1·5-litre flask together with zinc turnings (20 g.) and heat was applied until the reaction commenced. After this had subsided, the liquid was boiled under reflux for ¾ hour, cooled, decanted from undissolved zinc, and shaken with dilute sulphuric acid. The yellow benzene solution was dried over anhydrous sodium sulphate, the solvent removed on the steam-bath, and the residual light yellow oil, consisting of crude ethyl β-veratryl-β-hydroxybutyrate (p. 2992), distilled twice under diminished pressure; the resulting *ethyl β-veratrylcrotonate* (50 g.), b. p. 195—196°/10 mm., crystallised from ligroin in large colourless prisms, m. p. 51—52° (Found: C, 67·1; H, 7·1. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·2%).

In another experiment, ethyl β-veratryl-β-hydroxybutyrate (50 g.) was refluxed in dry benzene (200 c.c.) with phosphorus oxychloride (15 c.c.) for 30 minutes. The benzene solution, which turned dark red, was washed with water and dried over sodium sulphate, and the solvent removed on the steam-bath. The dark red oil, distilled under diminished pressure, gave ethyl β-veratrylcrotonate (30 g.), and a residue which could not be distilled without decomposition. This was hydrolysed with alcoholic potassium hydroxide and the solution was diluted with water, concentrated under diminished pressure on the steam-bath, and acidified; an amorphous mass then separated which, after solution in bicarbonate, extraction with ether and chloroform, and reprecipitation, could ultimately be obtained crystalline from methyl alcohol, separating in colourless prisms, m. p. 225—226° (Foun

C, 64·8; H, 6·5; *M*, in camphor by Rast's method, 482. $C_{24}H_{28}O_8$ requires C, 64·8; H, 6·3%; *M*, 444). This *substance*, which does not appear to be reduced by sodium amalgam, is evidently produced from two molecules of veratrylhydroxybutyric acid by the elimination of two molecules of water ($2C_{12}H_{16}O_5 - 2H_2O = C_{24}H_{28}O_8$). The amount of available material was, however, so small that no further experiments were made with the substance.

β-*Veratrylcrotonic acid* (VII) was prepared by refluxing the ester (155 g.) with alcohol (500 c.c.), water (40 c.c.), and potassium hydroxide (42 g.) for 2 hours. The solution was diluted with twice its bulk of water, concentrated under diminished pressure on the steam-bath, and acidified with hydrochloric acid; the crude brown *acid* (120 g.) obtained crystallised from benzene in pointed prisms, m. p. 138—140° (Found: C, 64·7; H, 6·3. $C_{12}H_{14}O_4$ requires C, 64·8; H, 6·3%). It is sparingly soluble in water but readily soluble in the usual organic solvents with the exception of petroleum. The solution in concentrated sulphuric acid is yellow and exhibits a greenish fluorescence on standing.

The aqueous and the benzene mother-liquor (above) contain considerable quantities of a second acid which has not yet been carefully examined; it melts at 90—95° and is probably a stereoisomeride (compare Johnson and Kon, J., 1926, 2749).

β-*Veratrylbutyric Acid* (VIII).—β-Veratrylcrotonic acid (90 g.), dissolved in water (2·5 l.) and sodium hydroxide (17 g.), was treated with sodium amalgam (4 kg. of 4%) at 85—90° with mechanical stirring. After 12 hours, the cooled and filtered solution was nearly neutralised with hydrochloric acid, and a cold aqueous solution of permanganate (100 c.c. of 1%) added. After a few minutes, sulphur dioxide in excess was passed in and the white precipitate of the acid was collected, washed well, dried in a vacuum desiccator, and crystallised from benzene, separating in pointed prisms (Found: C, 64·2; H, 7·1. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·1%).

β-*Veratrylbutyric acid* melts at 84—85° and is very soluble in methyl alcohol but sparingly soluble in water or petroleum. It separates from dilute acetic acid in slender elongated prisms containing $1H_2O$: these melt at about 60—61° and lose water at 100°; the solid remaining melts at 84—85° (Found: loss at 100°, 8·3. $C_{12}H_{16}O_4,H_2O$ requires H_2O, 7·5%).

5 : 6-*Dimethoxy-3-methyl-1-hydrindone* (IX).—β-Veratrylbutyric acid (7 g.) was mixed with concentrated sulphuric acid (30 c.c.) at 60°. The temperature rose to 73° and was maintained at that for 3 minutes; the deep red solution was then poured on ice and extracted with chloroform. After being washed with sodium carbonate

and the solvent removed; the colourless gum obtained soon crystallised and separated from very dilute methyl alcohol, on long standing, in almost colourless prisms, m. p. 90—91° (Found: C, 69·6; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

This *hydrindone* is very soluble in organic solvents with the exception of petroleum. The *oxime*, prepared by the action of hydroxylamine hydrochloride and potassium acetate on an alcoholic solution of the hydrindone, is readily soluble in methyl alcohol and separates, on the addition of water, as a felted mass of colourless elongated prisms, m. p. 128—129° with previous softening (Found: N, 6·4. $C_{12}H_{15}O_3N$ requires N, 6·3%). The iso*nitroso*-derivative was prepared by the action of methyl nitrite on an alcoholic solution of the hydrindone containing a little hydrochloric acid. It separated from methyl alcohol, in which it was rather sparingly soluble, in faintly lemon-coloured prisms, m. p. 225—226° (decomp.) (Found: N, 5·6. $C_{12}H_{13}O_4N$ requires N, 6·0%).

6-*Bromo*-β-*veratrylbutyric Acid* (X).—β-Veratrylbutyric acid (75 g.) was dissolved in glacial acetic acid (150 c.c.) and acetic anhydride (50 c.c.) at 0° and mechanically stirred while bromine (55 g.) in glacial acetic acid (50 c.c.) was slowly added. The product was poured into water containing a little sulphurous acid. The almost colourless oil (100 g.) obtained gradually solidified; after being washed, it was dried in a desiccator and a portion was crystallised from acetic acid and a little water, separating in colourless stout prisms, m. p. 106—107° (Found: C, 47·5; H, 5·0. $C_{12}H_{15}O_4Br$ requires C, 47·5; H, 5·0%). This *bromo-acid* is very soluble in organic solvents with the exception of petroleum and may be crystallised from a mixture of this and benzene.

4-*Bromo*-6 : 7-*dimethoxy*-3-*methyl*-1-*hydrindone* (XI).—6-Bromo-β-veratrylbutyric acid (10 g.) was treated with concentrated sulphuric acid (50 c.c.) at 75° for 5 minutes and the orange-red solution was then poured on ice and extracted with chloroform. After being washed with sodium carbonate solution, the extract was dried over anhydrous potassium carbonate, and the solvent removed. The light green gum obtained partly crystallised when rubbed with a glass rod. After draining on porous porcelain and several crystallisations from dilute methyl alcohol, the *bromohydrindone* was obtained in lemon-coloured, flat prisms (2 g.), m. p. 82—83° (Found: C, 50·5; H, 4·6. $C_{12}H_{13}O_3Br$ requires C, 50·5; H, 4·6%). The *oxime* separated from methyl alcohol in stout prisms, m. p. 187—188° (Found: N, 4·5. $C_{12}H_{14}O_3NBr$ requires N, 4·7%).

4-*Bromo*-2-*isonitroso*-6 : 7-*dimethoxy*-3-*methyl*-1-*hydrindone* (XII).—A solution of the bromohydrindone (5 g.) in methyl alcohol (30 c.c.) and concentrated hydrochloric acid (2 c.c.) was saturated

with methyl nitrite, the temperature being maintained at 35°. The yellow solution obtained slowly deposited crystals of the iso*nitroso*-derivative, which separated from alcohol, in which it was but slightly soluble, in small, pale yellow, elongated prisms (3·5 g.), m. p. 217° (decomp.) (Found : N, 4·3. $C_{12}H_{12}O_4NBr$ requires N, 4·4%). The acid mother-liquor, on being concentrated in a vacuum, deposited a crystalline substance (1 g.), which separated from methyl alcohol in colourless prisms, m. p. 155—156°, but was not further examined.

6-Bromo-3 : 4-dimethoxy-α-methylhomophthalic Anhydride (XV).—The *iso*nitroso-derivative (3·7 g.) was dissolved in water (25 c.c.) and sodium hydroxide (1·7 g.), toluene-*p*-sulphonyl chloride (2·7 g.) added to the deep red solution, and the mixture well shaken. On raising the temperature gradually to 50°, all went into solution, and at 60° the liquid became colourless. It was cooled, filtered, and acidified and the colourless syrupy 6-bromo-2-carboxy-3 : 4-dimethoxy-α-phenylpropionitrile (XIII), which did not crystallise, was extracted with ether. After removal of the solvent, the gummy nitrile was gently boiled with aqueous sodium hydroxide (50 c.c. of 8%) for 3 hours or until evolution of ammonia could no longer be detected. The filtered and well-cooled solution deposited, on addition of hydrochloric acid, crude 6-bromo-3 : 4-dimethoxy-α-methylhomophthalic acid (XIV) as a sticky mass; this was extracted with ether, and the ethereal solution dried over anhydrous sodium sulphate and evaporated. The colourless gummy acid was refluxed on the steam-bath with excess of acetyl chloride for ½ hour, the excess of acetyl chloride removed under diminished pressure, and the pale yellow *anhydride* (XV) crystallised from dry benzene, separating in minute, colourless, flat prisms (2·8 g.), m. p. 128—129° (Found : C, 45·7; H, 3·5. $C_{12}H_{11}O_5Br$ requires C, 45·7; H, 3·5%).

3 : 4-Dimethoxy-α-methylhomophthalic Anhydride (XVII).—The bromo-anhydride just described (2 g.) was dissolved in a little dilute aqueous sodium hydroxide, and the yellow solution warmed for a few minutes on the steam-bath until colourless. It was then diluted with water (100 c.c.) and heated on the steam-bath with sodium amalgam (100 g. of 4%) for 6 hours until a small filtered test portion showed only a faint cloudiness on treatment with hydrochloric acid. The whole was then acidified, extracted several times with ether, saturated with ammonium sulphate, and again repeatedly extracted, and the combined extracts were carefully dried over anhydrous sodium sulphate. The colourless gummy 3 : 4-dimethoxy-α-methylhomophthalic acid remaining after evaporation of the ether was refluxed with excess of acetyl chloride for ½ hour. After removal of the excess of acetyl chloride under diminished pressure,

he pale brown 3 : 4-*dimethoxy-α-methylhomophthalic anhydr* XVII) was dissolved in boiling dry benzene and the solution v lecolorised with norite and concentrated; the anhydride tt eparated in colourless prisms (1·2 g.), m. p. 131—133° (Foun), 60·8; H, 5·1. $C_{12}H_{12}O_5$ requires C, 61·0; H, 5·1%).

6 : 7 : 3′ : 4′-*Tetramethoxy-9-methyl-2′-carbomethoxy-3 : 4-dihyd rotopapaverine* (XIX).—3 : 4-Dimethoxy-α-methylhomophtha nhydride (1·5 g.) and β-veratrylethylamine (1·3 g.) were reflux ogether in dry benzene (30 c.c.) for 2 hours. The well-cooled, p ellow solution was extracted with aqueous sodium hydrox 25 c.c. of 5%) and the orange-yellow alkaline liquid was extract vith ether and then made acid with hydrochloric acid. T recipitated, colourless, gummy *N*-β-veratrylethyl-3 : 4-dimetho :-methylhomophthalamic acid (XVIII) was dried in a desiccat ınd the brittle amorphous solid obtained, which could not rystallised, was dissolved in a solution of sodium bicarbon 0·7 g.) in water (10 c.c.). Addition of silver nitrate (3 g. in 10 of water) to the filtered solution precipitated the silver salt, wh was washed once with water, dried in a vacuum over phosph oxide, and refluxed with methyl iodide (3 c.c.) in dry ether (50 c or 12 hours. The filtered ethereal solution was evaporated lryness and the crude gummy methyl ester (2 g.) was gently bo with freshly distilled phosphorus oxychloride (20 c.c.) for 10 minu The excess of oxychloride was removed by distillation under redu pressure, the residue warmed with water (60 c.c.), and the c solution made alkaline with sodium hydroxide; the orange an phous precipitate which then separated crystallised from met alcohol in colourless prisms (1·1 g.), m. p. 136—137° with previ softening (Found: C, 66·7; H, 6·5. $C_{23}H_{27}O_6N$ requires C, 6 H, 6·5%). This *substance*, the properties of which show that it the constitution (XIX), is soluble in dilute acids and precipita unchanged by alkalis. It does not appear to be readily hydroly by methyl-alcoholic sodium hydroxide.

Oxydehydrocorydaline (XX).—When the methyl ester (XIX) described (1 g.) was heated in a test-tube at 150—170° for 10 minu the colourless substance, after melting, turned yellow, evolutio methyl alcohol could be detected, and the residue became quite and apparently crystalline. The substance was dissolved in m boiling alcohol, in which it was very sparingly soluble; aln colourless, cube-like prisms separated on slow cooling, and a furt quantity was obtained by concentrating the mother-liquor. A recrystallisation, the substance (0·5 g.) melted at 235—236° an micro-analysis gave C, 69·0; H, 6·0, whereas $C_{22}H_{23}O_5N$ requ

alkalis, but dissolves readily in warm glacial acetic acid, and crystallises unchanged on the addition of water. It is soluble in sulphuric acid (50%), on warming, and the addition of a drop of concentrated nitric acid produces an almost black coloration, which changes to deep wine-red in a few minutes and then very slowly fades to yellow. There could be no doubt that this substance, which has properties so very similar to those of oxyberberine, is oxydehydrocorydaline (XX), and this view was confirmed, as has already been explained in the introduction (p. 2994), by direct comparison with a specimen of oxydehydrocorydaline from corydaline for which we are indebted to Dr. von Bruchhausen.

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CCCXCIV.—*The Dependence of Rotatory Power on Chemical Constitution. Part XXXIII. The Resolution of* dl-m-*Carboxyphenyl Ethyl Sulphoxide and of* dl-m-*Carboxyphenylethylsulphine*-p-*toluenesulphonylimine.*

By JOSEPH HOLLOWAY, JOSEPH KENYON, and HENRY PHILLIPS.

THE resolution of the sulphoxide (I) and the sulphilimine (II) derived from *m*-carboxyphenyl ethyl sulphide substantiates the

$$\text{(I)}\quad \overset{-}{O}-\overset{+}{S}\!\!<\!\!{C_6H_4\cdot CO_2H \atop C_2H_5} \qquad\qquad C_6H_4Me\cdot SO_2\cdot\overset{-}{N}-\overset{+}{S}\!\!<\!\!{C_6H_4\cdot CO_2H \atop C_2H_5}\quad \text{(II)}$$

results previously recorded (Harrison, Kenyon, and Phillips, J., 1926, 2079; Clarke, Kenyon, and Phillips, J., 1927, 188), which provided independent experimental evidence for the existence of semipolar double bonds.

The brucine salt of m-*carboxyphenyl ethyl sulphoxide*, after recrystallisation from ethyl alcohol until no further increase in rotatory power occurred, had $[\alpha]_{5461}^{20^\circ}$ $+70^\circ$ in chloroform solution. It gave on decomposition with aqueous sodium hydroxide *d*-*m*-carboxyphenyl ethyl sulphoxide the specific rotatory powers of which are recorded in Table I.

The quinidine salt of the *dl*-sulphoxide, after recrystallisation from benzene, containing a little ethyl alcohol, until constancy of rotatory power—$[\alpha]_{5461}^{20^\circ}$ $+102^\circ$—was reached, gave on decomposition *l*-*m*-carboxyphenyl ethyl sulphoxide with $[\alpha]_{5461}^{20^\circ}$ -232° in chloroform solution. The satisfactory agreement between the specific rotatory

are

TABLE I.

Specific rotatory powers of *d*-*m*-carboxyphenyl ethyl sulphoxide in solvents at 25°.

c = g. of sulphoxide in 100 c.c. of solution; l = 2.

Solvent.	c.	λ 6708.	5893.	5790.	5461.	4358.
Methyl alcohol	2·7500	+126°	+165°	+171°	+202°	+418°
Chloroform	4·2250	150	202	211	236	445
Ethyl alcohol	4·0985	217	255	260	287	465
Pyridine	1·5750	167	238	251	282	460

Specific rotatory power of the potassium salt of *d*-*m*-carboxyphenyl ethyl sulphoxide.

Water *	1·2650	113	153	160	180	355

* This solution was prepared by diluting to the required volume a solution of a known weight of the *d*-sulphoxide in the calculated quantity of standard potassium hydroxide.

The specific rotatory powers of *d*-*m*-carboxyphenyl ethyl sulphoxide under the experimental conditions employed are all greater than those of *d*-*m*-carboxyphenyl methyl sulphoxide (Harrison, Kenyon, and Phillips, *loc. cit.*), but in common with the optically active sulphoxide previously described it exhibits complex rotatory dispersion and gives solutions which show no sign of mutarotation even after standing for several months. It can be concluded that the *dl*-sulphoxide is a racemic compound, since its m. p. and its solubilities in various solvents differ widely from those of the optically active enantiomorphs. The *d*-sulphoxide on oxidation yields optically inactive m-*carboxyphenylethylsulphone.*

Under experimental conditions which lead to the replacement of the oxygen atom of the *d*-sulphoxide, racemisation occurs. For example, when the sulphoxide is treated in chloroform solution with hydrogen bromide, the resulting m-*carboxyphenyl ethyl sulphide dibromide* is optically inactive. Further, the rotatory power of a solution of the *d*-sulphoxide in 1·1N-hydrobromic acid remains practically unchanged during 1588 hours, but in the same time, owing presumably to more complete reversible replacement of the oxygen atom by bromine, a similar solution in 3·3N-hydrobromic acid loses its optical activity as shown in Table II.

TABLE II.

Specific rotatory powers of *d*-*m*-carboxyphenyl ethyl sulphoxide in 3·3N-hydrobromic acid solution at 25°.

m - *Carboxyphenylethylsulphine* - p - *toluenesulphonylimine.* — Th brucine salt of *dl-m*-carboxyphenylethylsulphine-*p*-toluenesulphony imine on recrystallisation from acetone changed rapidly in rotator power and when optically pure had $[\alpha]_{5461}^{25^\circ}$ −157° in ethyl-alcohol solntion. On decomposition of this salt with dilute hydrochlor acid l-m-*carboxyphenylethylsulphine*-p-*toluenesulphonylimine* was ob tained, the specific rotatory powers of which are recorded i Table III.

TABLE III.

Specific rotatory powers of *l-m*-carboxyphenylethylsulphine-*p*-toluenesulphonylimine in solvents at 25°.

$l = 2$; c = g. of *l*-sulphilimine in 100 c.c. of solution.

Solvent.	c.	λ 6708.	5893.	5790.	5461.	435
Ethyl alcohol	2·7725	−226°	−308°	−324°	−373°	−69(
Ethyl acetate	0·8980	213	286	307	343	64(
Chloroform	1·2315	243	300	322	365	67ξ
,, ...	0·6380	—	—	305	345	64:
,, ...	0·5600	204	272	286	330	62]
Glacial acetic acid ...	1·9185	233	280	306	334	64:
Pyridine	2·5695	200	290	307	344	67(

Specific rotatory power of the sodium salt of *l-m*-carboxypheny ethylsulphine-*p*-toluenesulphonylimine.

Water *	1·7950	—	—	318	363	66:

* This solution was prepared by diluting to the required volume a soluti of a known weight of the *l*-sulphilimine in the calculated quantity of standa sodium hydroxide.

The more soluble portions of the brucine salt on decompositi gave a sulphilimine with $[\alpha]_{5461}$ +270°. This sulphilimine w combined with strychnine, and the strychnine salt crystallis repeatedly from ethyl alcohol until its rotatory power remain unchanged. It then had $[\alpha]_{5461}^{25^\circ}$ +152° and on decomposition ga *d-m*-carboxyphenylethylsulphine-*p*-toluenesulphonylimine with [α] +373° in ethyl-alcoholic solution.

The physical properties of both optically active and the inact sulphilimines are similar, in marked contrast to the wide divergen between the physical properties of the optically active and inact sulphoxides. Hence the *dl*-sulphilimine is probably a mixture the two enantiomorphs and not a racemic compound. The spec rotatory power of the optically active sulphilimine is but sligh influenced by solvents and remains unchanged when the soluti are kept for several months. The rotatory dispersion is less comp than that exhibited in corresponding solvents by the sulphoxi in ethyl-alcoholic solution the sulphilimine exhibits simple rotati

dispersion, since a straight line is obtained when $1/\alpha$ is plotted against λ^2.

$d + dl$-*m*-Carboxyphenylethylsulphine - *p* - toluenesulphonylimine was converted by the action of dilute hydrochloric acid into a mixture of *p*-toluenesulphonamide, *m*-carboxyphenyl ethyl sulphide, and *dl*-*m*-carboxyphenyl ethyl sulphoxide, and with hydrogen peroxide the *dl*-sulphilimine gave as sole products *p*-toluenesulphonamide and *m*-carboxyphenylethylsulphone.

EXPERIMENTAL.

Preparation and Resolution of dl-m-*Carboxyphenyl Ethyl Sulphoxide.*

m-*Ethylthiolbenzoic Acid.*—*m*-Thiolbenzoic acid (78 g.), prepared by the reduction of *m*-chlorosulphonylbenzoic acid (Smiles and Stewart, J., 1921, **119**, 1792), was dissolved in sodium hydroxide solution (1000 c.c. of 10%) and added to a solution of ethyl *p*-toluenesulphonate (200 g.) in ethyl alcohol (500 c.c.). The mixture was heated under reflux on a steam-bath until a sample remained clear on dilution with water (6—8 hrs.). m-*Ethylthiolbenzoic acid*, precipitated from the cold reaction mixture by hydrochloric acid, was recrystallised twice from aqueous alcohol, from which it (73 g.) separated as shining leaflets, m. p. 99—100° (Found: equiv., by titration, 181. $C_9H_{10}O_2S$ requires equiv., 182).

dl-m-*Carboxyphenyl Ethyl Sulphoxide.*—*m*-Ethylthiolbenzoic acid (78 g.) and 2*N*-nitric acid (780 c.c.) were heated on a steam-bath until solution was almost complete and the evolution of nitrous fumes had ceased. The cold filtered solution was extracted several times with chloroform. The dl-m-*carboxyphenyl ethyl sulphoxide* obtained on evaporation of the dried chloroform extract was crystallised from either benzene or a mixture of chloroform and ligroin; it (52 g.) then had m. p. 104—106° (Found: C, 54·6; H, 5·1; S, 16·2; equiv., by titration, 199. $C_9H_{10}O_3S$ requires C, 54·5; H, 5·0; S, 16·1%; equiv., 198). It is moderately easily soluble in hot water, more easily soluble in warm alcohol, acetone, or chloroform, and fairly readily soluble in warm benzene, cold chloroform, or cold alcohol.

d-m-*Carboxyphenyl Ethyl Sulphoxide.*—When a solution of the *dl*-sulphoxide (27·5 g.) and brucine (55 g.) in hot ethyl alcohol (50 c.c. of 99%) was allowed to cool, the brucine salt, m. p. 98—101°, separated as rosettes of needles. After five recrystallisations from alcohol, subsequent recrystallisation produced no further change in the rotatory power of the salt, which then had m. p. 125—126° (after desiccation for 3 days) and $[\alpha]_{5461}$ +69° (c = 2·145,

solution, the liberated brucine removed by filtration, and the filtrate acidified and extracted three times with chloroform. *d-m*-Carboxyphenyl ethyl sulphoxide, obtained from the dried chloroform extract, set to a hard mass of crystalline needles, m. p. 71°, and $[\alpha]_{5461}^{25°}$ +236° (l = 2, c = 2·230) in chloroform solution.

l-m-*Carboxyphenyl Ethyl Sulphoxide.*—The *dl*-sulphoxide (15 g.) and quinidine (25 g.) were dissolved in hot benzene (150 c.c.) containing a few drops of ethyl alcohol. The quinidine salt (10 g.), which separated on standing, had m. p. 189°, $[\alpha]_{5461}$ +130° (l = 2, c = 1·25) in chloroform solution. After five further recrystallisations, the optically pure salt was obtained with m. p. 198—199° and $[\alpha]_{5461}$ +102° (l = 2, c = 1·25) in chloroform solution. *l-m*-Carboxyphenyl ethyl sulphoxide, obtained by the decomposition of this quinidine salt, had $[\alpha]_{5461}^{25°}$ −232°, $[\alpha]_{5790}^{25°}$ −207°, $[\alpha]_{4358}^{25°}$ −440° (l = 2, c = 1·25) in chloroform solution.

m-*Carboxyphenylethylsulphone.*—The calculated quantity of perhydrol was added to a solution of *m*-ethylthiolbenzoic acid in aqueous potassium carbonate. When reaction was complete, the solution was cooled, filtered, and acidified with concentrated hydrochloric acid. The precipitated m-*carboxyphenylethylsulphone*, after crystallisation from hot water, had m. p. 162—164° (Found: *equiv., by titration, 210.* $C_9H_{10}O_4S$ *requires equiv., 214), and was* identical with the inactive sulphone, prepared in a similar manner from *d-m*-carboxyphenyl ethyl sulphoxide.

m-*Carboxyphenyl ethyl sulphide dibromide* separated as clusters of yellowish-red needles, m. p. 102°, when bromine (13 g.) was added to *m*-ethylthiolbenzoic acid (9 g.) in carbon disulphide (100 c.c.) (Found: Br, 45·3. $C_9H_{10}O_2SBr_2$ requires Br, 46·8%). Its bromine content decreases on exposure to air.

Preparation and Resolution of dl-m-*Carboxyphenylethylsulphine*-p-*toluenesulphonylimine.*

dl-m-*Carboxyphenylethylsulphine*-p-*toluenesulphonylimine.*—To a solution of *m*-ethylthiolbenzoic acid (110 g.) in warm alcohol (550 c.c.), made just alkaline to phenolphthalein by the addition of 3*N*-sodium hydroxide, chloramine-T (197 g.; 1·1 mols.) in warm water (550 c.c.) was added, and the mixture heated under reflux on a steam-bath for 2 hours. Dilute hydrochloric acid was added to the resulting solution when cold; dl-m-*carboxyphenylethylsulphine*-p-*toluenesulphonylimine* (100 g.) separated, and was obtained as small needles, m. p. 149°, by crystallisation from aqueous alcohol (Found: C, 54·8; H, 4·8; N, 3·9; S, 18·0; equiv., by titration, 349.

l-m-*Carboxyphenylethylsulphine*-p-*toluenesulphonylimine*.—To the *dl*-sulphonylimine (45 g.) in acetone (150 c.c.) containing a little ethyl alcohol, brucine (55 g.) was added, and the mixture warmed until solution was complete. The brucine salt, which crystallised in rosettes of fine needles, m. p. 160—161°, on cooling, was recrystallised from four successive quantities (about 150 c.c. in each case) of acetone containing a little alcohol. Subsequent recrystallisation produced no further alteration in the rotatory power of this salt, which then had m. p. 161°, and $[\alpha]_{5461}^{20^\circ}$ −157° and $[\alpha]_{4359}^{20^\circ}$ −287° (l = 2, c = 1·100) in ethyl-alcoholic solution.

The brucine salt, dissolved in warm alcohol, was added to dilute hydrochloric acid, and a current of air drawn through the resulting clear solution. The l-m-*carboxyphenylethylsulphine*-p-*toluenesulphonylimine* which separated crystallised from alcohol in small prismatic needles, m. p. 149—150°, and had $[\alpha]_{5461}^{25^\circ}$ −368° (l = 2, c = 2·543) in ethyl-alcoholic solution (Found : C, 54·8; H, 4·8%).

Isolation of d-m-*Carboxyphenylethylsulphine*-p-*toluenesulphonylimine*.—(a) *By means of cinchonidine.* The *d* + *dl*-*m*-carboxyphenylethylsulphine-*p*-toluenesulphonylimine recovered from the alcohol–acetone mother-liquor from the first crystallisation of the brucine salt described above had $[\alpha]_{5461}$ +243°. That obtained from a second preparation of the brucine salt had $[\alpha]_{5461}$ +279°. These two lots (17·8 g.) of highly dextrorotatory sulphilimine, together with cinchonidine (14·9 g.), were dissolved in hot alcohol (500 c.c.). On cooling, the cinchonidine salt separated in bulky clusters of prismatic needles. It was recrystallised eight times from alcohol, but purification was rather slow and, towards the end, somewhat erratic. The almost optically pure *l*-cinchonidine *d*-*m*-carboxyphenylethylsulphine-*p*-toluenesulphonylimine obtained had m. p. 198—199° and $[\alpha]_{5461}^{20^\circ}$ +50° (l = 2, c = 1·050) in chloroform solution. On decomposition, as previously described, it gave *d* + *dl*-*m*-carboxyphenylethylsulphine-*p*-toluenesulphonylimine, m. p. 149—150°, $[\alpha]_{5461}^{20^\circ}$ +364° (l = 2, c = 2·070) in ethyl-alcoholic solution.

(b) *By means of strychnine.* On cooling a solution of the *d* + *dl*-sulphilimine (5·3 g.; $[\alpha]_{5461}$ +270°) and strychnine (5·0 g.) in alcohol (20 c.c.), the strychnine *d*-salt, m. p. 165°, separated. It was recrystallised ten times from alcohol (90—50 c.c.), its rotatory power then being constant, and was thus obtained as glistening prismatic needles, m. p. 174° (decomp.), $[\alpha]_{5461}^{25^\circ}$ +152° (l = 2, c = 0·9566) in ethyl-alcoholic solution. On decomposition with dilute sulphuric acid it gave *d*-*m*-carboxyphenylethylsulphine-*p*-toluenesulphonylimine, m. p. 150—151°, $[\alpha]_{5780}^{20^\circ}$ +323°, $[\alpha]_{5461}^{20^\circ}$ +373°, $[\alpha]_{4359}^{25^\circ}$ +689° (l = 2, c = 2·3425) in ethyl-alcoholic solution.

It is somewhat curious that, although strychnine forms

fully crystalline salt—hard rosettes of fine needles—m. p. 162—164°, with the *dl*-sulphilimine, yet crystallisation of this salt from methyl alcohol effects no separation of the diastereoisomeric forms.

The Interaction of l + dl-m-*Carboxyphenylethylsulphine*-p-*toluenesulphonylimine and Hydrochloric Acid.*—The clear, deep red solution obtained by heating *l* + *dl*-sulphilimine (6 g.) with concentrated hydrochloric acid (18 c.c.) on a steam-bath for 5 minutes was neutralised with sodium carbonate solution, and the precipitated *p*-toluenesulphonamide (2·5 g., m. p. 138°) removed. The filtrate was acidified and the *m*-ethylthiolbenzoic acid liberated (1 g.), after crystallisation from aqueous alcohol, had m. p. 99°. By extraction five times with chloroform, the *m*-carboxyphenyl ethyl sulphoxide (1·0 g., m. p. 102—104°) remaining in the filtrate was isolated: 0·5 g. made up to 20 c.c. with chloroform gave a solution which was optically inactive when examined in a 2-dcm. tube in light of λ5461. The total yield of hydrolytic products was 75% of the calculated quantity.

The Interaction of dl-m-*Carboxyphenylethylsulphine*-p-*toluenesulphonylimine and Hydrogen Peroxide.*—A mixture of the *dl*-sulphilimine (4 g.) and perhydrol (35 c.c.), heated on a steam-bath with occasional shaking, gave a clear solution in 15 minutes. The crystalline material (3 g., m. p. indefinite) which separated on cooling was recrystallised from a small bulk of ethyl alcohol, glistening leaflets (1·5 g., m. p. 162—164°) of *m*-carboxyphenylethylsulphone being obtained. After dilution, the filtrate yielded a second crop of crystals (0·5 g.) which proved to be *p*-toluenesulphonamide, m. p. 138°.

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CCCXCV.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XXVI. The Optical Activity of Malic Acid in the Presence of Sodium Molybdate.*

By THOMAS STEWART PATTERSON and CHARLES BUCHANAN.

IN connexion with earlier work by one of us on the general problem of the rotation of optically active compounds, in which the influence

studied, we thought it worth while to investigate some of those remarkable cases discovered by Biot and by Gernez in which substances such as borax and salts of molybdic and tungstic acids greatly influence the rotation of certain compounds like malic acid and tartaric acid. Perhaps the most remarkable effects of this character are those recorded by Gernez (*Compt. rend.*, 1889, **109**, 769), who studied solutions in which, to a fixed quantity of malic acid, gradually increasing amounts of sodium molybdate were added. He found the rotation to vary in such a manner that two minima of negative rotation and one positive maximum were developed, whilst between these three different concentrations were observed at which the rotation was zero. Gernez accounted for this behaviour by assuming that each maximum or minimum corresponds to the formation of a definite additive compound having a composition represented by the relative amounts of malic acid and sodium molybdate in solution at that particular concentration.

A summary of further work on this subject is given by Darmois (*J. Phys. Radium*, 1923, **4**, 49), who claims to have isolated three compounds: $(MoO_4)_2C_4H_6O_4Na_2,3H_2O$, with $[\alpha]_{5780}$ $+184°$ ($c = 0{\cdot}95$); $MoO_3,2C_4H_6O_5,2NaOH$, $[\alpha]_{5780}$ $-55{\cdot}1°$ ($c = 20$); and $MoO_3,2C_4H_6O_5,4NaOH$, for which no rotation value seems to be given.

The interesting phenomena described by Gernez have hitherto only been examined by means of light of one refrangibility and, with one exception, at the ordinary temperature,* and we deemed it of interest to investigate a number of these solutions at different temperatures and for different colours of light, especially for those concentrations at which the rotation changes from a positive to a negative value through zero, and *vice versa*, with increasing concentration of molybdic acid.

Preparation of Solutions.—The malic acid used was recrystallised from water and made thoroughly anhydrous. It had m. p. 100—103°, $[\alpha]^{17°}_{5780}$ $-1{\cdot}99°$ (1·861 g. in 20 c.c. of water); Gernez found $-2{\cdot}0°$ at the same temperature for *sodium* yellow (λ 5890).

Our first series of solutions was made up to correspond to those of Gernez, who used 1·1166 g. of malic acid in 12 c.c. of water. A

* Grossman and Pötter (*Z. physikal. Chem.*, 1906, **56**, 577) examined solutions containing malic acid and sodium molybdate up to temperatures of 95° and concluded that various complexes are formed, some dextro and some lævo, which on dilution decompose, yielding a complex of one molecule of Na_2MoO_4 and one molecule of malic acid. The work to be described, however, shows that above 60° such solutions undergo permanent change. They turn blue, and on cooling the rotation does not revert to its original value. Darmois (*loc. cit.*, pp. 63, 60) states that he used three different colours of light, but he

solution of malic acid in water was prepared of as nearly as possib 18·61 g. in 100 c.c. of solution, and its strength determined acc rately by titration. Various quantities of sodium molybda ($Na_2MoO_4,2H_2O$; recrystallised from water) were weighed into 20 c.c. graduated flask to which 10 c.c. of the malic acid solutio were added, and the solution was made up to 20 c.c. with wate The rotation of each solution was then examined for several colou of light and usually at different temperatures. The specific rotatio was calculated relative to the amount of malic acid in the solutio $[\alpha] = 100\alpha/ldp$, where p = g. of malic acid per 100 g. of solutio or $[\alpha] = 100\alpha/lc$, where c = g. of malic acid per 100 c.c.

Fig. 1* shows the specific rotation for three colours of light at 1 plotted relative to *concentration of sodium molybdate*, the quanti of malic acid present remaining, of course, constant throughout.

The specific rotation of the malic acid solution without additi is so small that it can hardly be indicated on the diagram, but th addition of sodium molybdate increases the negative rotation ve rapidly, and almost linearly, for all three colours of light, unt the first minimum is reached with the addition of a quantity sodium molybdate corresponding to approximately 0·5 mol. p mol. of malic acid present in the solution (*A* in Fig. 1). On furth addition of molybdate the rotation then rapidly becomes le negative and reaches zero at a concentration of sodium molybda corresponding to about 0·7 mol. per mol. of malic acid. Ze rotation is not reached, however, at exactly the same concentratio of molybdate for each colour of light; the three curves do not intersect on the line of zero rotation (*B* in Fig. 1).

With further addition of molybdate the rotation rapidly ris again, almost linearly, and reaches a positive maximum at or ne a concentration of 1 mol. of molybdate per mol. of malic ac (*C* in Fig. 1). The rotation then rapidly diminishes, passing throu zero rotation at *D*, where the concentration of molybdate is 1·4 mol per mol. of malic acid, but it is difficult to decide whether the ze for all three colours is at the same concentration. The three curv appear to intersect in a region where the rotation has a slight negati value of about $-4°$; the diagram does not show this very wel With further addition of molybdate, a second minimum, *E*, reached at a concentration of about 1·75 mols. of molybdate 1 mol. of acid and, later, a third passage through zero rotation tak place at a concentration of about 2·07 mols. of molybdate to 1 acid. The rotation then increases steadily until no more molybda can be got into solution.

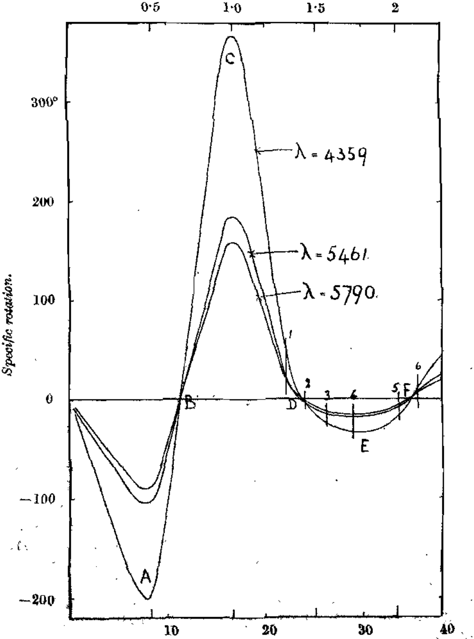
* To avoid confusion we have not indicated the individual experiment

These phenomena are very difficult to account for. It is easy to ay that various compounds are formed in solution between the nalic acid and the molybdate; but even on this hypothesis it is

FIG. 1.

Malic acid: c = 9·3; t = 17°.

Concentration of sodium molybdate in molecules per molecule of malic acid.



Concentration of sodium molybdate in grams per 100 c.c.

ifficult to give any consistent explanation of the phenomena. It light seem that at least four different kinds of combination must e postulated, with a reversal of sign of rotation between each

form. Any discussion of the matter can only be undertaken l making so many quite arbitrary assumptions that for the prese we do not propose to enter on it. The strongest argument in favo of this idea is that compounds of malic acid and sodium molybda can be isolated in the solid form, Darmois claiming to have isolate three, as already mentioned. An alternative suggestion is that tl sodium molybdate produces this effect by ordinary solvent actio and to show that this is not utterly improbable we may point to tl facts that (1) salts such as barium chloride, potassium bromid ammonium sulphate, etc., have very powerful depressing effec upon the rotation of aqueous solutions of ethyl tartrate (J., 191 **101**, 1834), and (2) ethyl tartrate dissolved in benzene, in tolue and in *o*- and *m*-xylene apparently exhibits in dilute solution bo a maximum and a minimum value in a manner not altogether unli this, although, of course, in very different degree (J., 1902, **81**, 109!

We wished particularly to examine the rotations of solutions the neighbourhood of the points *B*, *D*, and *F* (Fig. 1) as regards t effect of temperature change, since from our previous work we shou have expected, at these points, rapid change of rotation in corr spondence with the very rapid change of rotation due to alterati in concentration of the sodium molybdate.

Fig. 2* shows some of these temperature–rotation curves which a numbered to correspond to the numbers shown in Fig. 1. It w be noticed that in all cases change of temperature does produ rapid alteration of rotation, and also that this alteration of rotati with change in temperature is consistent.

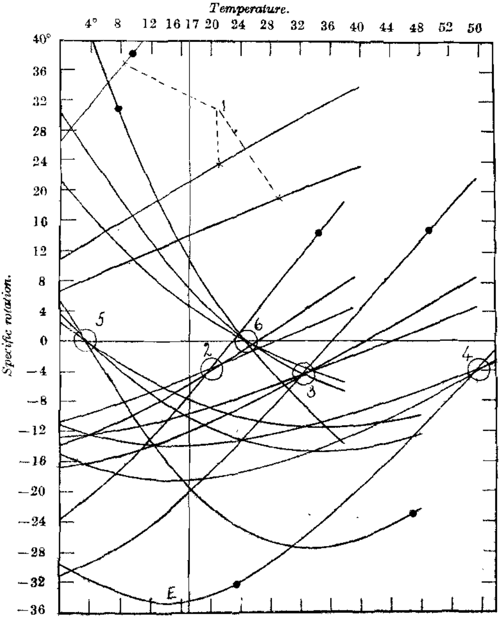
The general behaviour will be understood by considering t solutions marked 1, 2, 3, 4, 5, and 6 in Fig. 1. Of these, solution may be first considered. The data shown on Fig. 1 are those f a temperature of 17° as marked by a vertical line in Fig. 2. Wh this solution is cooled, the rotation diminishes and the curves spre out from one another, but when it is heated above 17° the curv rapidly approach each other and intersect at, or very near, a poi where the temperature is 20° and the specific rotation for the vario colours is in the neighbourhood of −4·0°. It is difficult to deci whether the curves meet accurately at a point or over a slight ran of temperature. On further heating of the solution, the rotati for all colours of light increases and the curves spread apart.

When solution 1 is heated the rotation for all the various colou of light rapidly increases, but clearly if it were possible to cool t solution much beyond zero, these curves would intersect one anoth

* It should be noted that only two of the curves in Figs. 1 and 2 are for t same wave-lengths. In Fig. 1, the third curve is for $\lambda = 5790$ (yellow) and late… Fig. 2, for $\lambda = 6234$ (red). This is not likely, however, to cause any confusio

at a lower temperature, which, since extrapolation would have to be carried out over a considerable range, cannot be estimated with accuracy.

FIG. 2.



Temperature-rotation curves for certain aqueous solutions of l-*malic acid and sodium molybdate, for* λ = 6234, 5461, 4359. *The curve for* λ = 4359 *is, in each case, marked with a black circle; the other two can then easily be identified. See also note on p.* 3010.

In solution 3 we find that, on heating from 0°, the rotation rapidly ncreases in such a way that the curves intersect one another at a emperature of approximately 33° and at a rotation value in the ieighbourhood of −4°, after which the rotation continues to increase, he curves spreading out as in other cases.

The data shown for solution 4 (the point E in Fig. 1) lie at the minimum of the concentration curve, and are represented at E in Fig. 2, and are of a particularly interesting character. On cooling, the rotation of this solution diminishes (becomes more negative) to show a distinct minimum and then rises again on further cooling to zero temperature. On heating, the curves show a behaviour very similar to that exhibited by those already dealt with: the rotation rapidly increases, and again the various curves intersect one another at the same rotation as before, namely $-4°$, but at a temperature of 55°. Thus when the three solutions 4, 3, and 2 are heated, the curves for the different colours of light are found to intersect at practically the same rotation value, but at gradually diminishing temperatures.

In solution 5 we find, as in the last case, distinct minima in the curves, but here the data shown in Fig. 1 at 5 lie on the left of the minimum in Fig. 2, whereas for solution 4 they lie to the right (point E, Fig. 2). On cooling, the curves for solution 5 gradually approach one another and intersect at a temperature of about $-4°$ and a rotation value in the neighbourhood of zero; on heating, the rotation diminishes and reaches a distinct minimum value, after which the curves rise again, but could not be followed to higher temperatures on account of the liability of the solution to decompose.

The temperature-rotation curves for solution 6 are also shown. In this case the rotation rapidly diminishes with rising temperature, and the curves intersect one another apparently over a slight range of temperature in the neighbourhood of zero rotation.

Thus, the behaviour throughout is entirely consistent; on heating the solutions 2, 3, and 4, the curves are made to intersect one another at practically the same rotation, $-4°$, but at different temperatures, viz., 20°, 33°, and 55° respectively. It seems indisputable that, on heating, these solutions are brought into the condition represented on Fig. 1 at the point D, and, from analogy, it will probably be admitted that when solution 1 is cooled, its temperature-rotation curves would be caused to intersect at this same point. On the other hand, by cooling solution 5 and by heating solution 6, the curves are caused to intersect at a rotation value at or very close to zero, but at temperatures of 4° and 24° respectively, and this region of intersection is that represented at F in Fig. 1.

We had hoped that with one of these solutions, such as number 4, we should be able to demonstrate both of these regions of intersection of the temperature-rotation curves: that by heating the solution we should be able to reach the point D on Fig. 1 and, by

is not possible to heat any of these solutions over a sufficient range of temperature.

It appears from this, however, that the behaviour of these solutions is closely similar to that of other simple active compounds dissolved in "indifferent" solvents, for it has been shown by one of us that, although the temperature–rotation curves of an active compound may be very greatly modified either by different solvents or by change of concentration in one solvent, yet the rotation value at which any two such curves intersect one another has, in general, one definite value, although it may occur at very different temperatures.

The data we have collected furnish interesting and unique material in connexion with the characteristic diagram. In a previous paper by one of us (J., 1916, **109**, 1202), it was suggested that in consequence of the apparently periodic character of the temperature–rotation curves for active compounds, "any given substance may very probably have several characteristic diagrams and several rational zeros. If these rational zeros are very different in value it might be possible readily to detect the trend of the two separate diagrams." And in a later paper (*Proc. Roy. Soc. Edinburgh*, 1918—19, **39**, 27) indications of the existence of two characteristic diagrams in the case of *iso*butyl dibenzoyltartrate were described. In the present instance, since there are four points (including the point of origin of the diagram) at which the rotation becomes zero, it might be possible to draw four separate characteristic diagrams. There should be one from the point of origin up to the region A; another from the region A through B to the region C; a third from the region C through D to the region E; and another from E through F onwards. Since the points of intersection lie so close to zero, it is not easy to distinguish clearly between these separate characteristic diagrams, but on account of the fact that the intersections at D and at F lie, quite definitely, (Fig. 2) at different rotation values, it is also certain that the two characteristic diagrams which could be drawn for these two regions of the curves are different. We do not wish to dwell upon the point now; we may have occasion to refer to it in connexion with later work. We may add, however, that in consequence of intersection taking place very near zero rotation in each case, dispersion ratios remain fairly constant throughout, the constancy being somewhat improved by calculating from the rational zero in each case.

If these curves are considered from the point of view of a combination of malic acid and sodium molybdate in solution, they might possibly be interpreted by supposing that heating the solutions has the effect of dissociating any compound which may be

The portion of the curve in the neighbourhood of the second minimum is possibly the most interesting on account of the comparatively easy recognisability of the two regions of intersection. We have not examined the other portions of the curve in so complete a fashion, but, except for solutions represented on the part of the curve from the origin up to A, it appears that heating the solutions causes a change of rotation similar to that obtained by travelling along the concentration curve to the left as in the cases referred to above. For solutions from the origin up to A, a different behaviour is noticeable: on heating such solutions it might be expected from the previous observations that the rotation should diminish, whereas the opposite takes place—the rotation increases slightly.

Since the number of colours of light used by us is only small, we have not examined very specially the dispersion curves for these solutions—they seem to us much like these for most other active compounds. By plotting λ^2 against $1/\alpha$ we find for the solution indicated by 1 in Figs. 1 and 2, at 16° and 36°, an approximately linear relationship, but for 2 and 3 at zero, 4 at 17° and 5 at 30°, this is not the case.

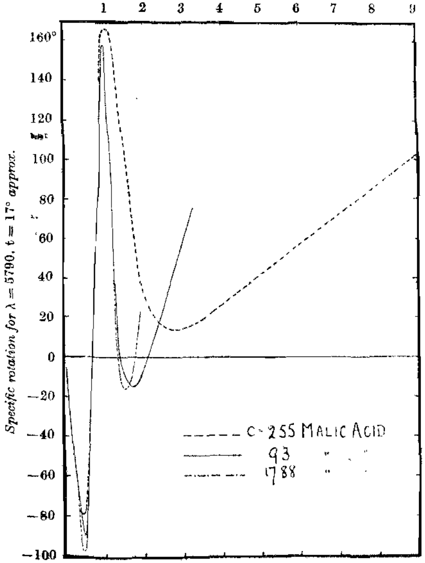
The foregoing experiments were carried out with practically the same concentration of malic acid as was used by Gernez, the concentration of sodium molybdate being increased as far as possible. In order to increase the proportion of molybdate to malic acid to a still greater extent, we used a more dilute solution of malic acid ($c = 2{\cdot}55$ g./100 c.c. of solution), the rotation being examined for three different colours of light at approximately 20°. The results for mercury yellow (λ 5790) are shown in Fig. 3. The curve obtained shows that the variation of the rotation for this proportion of malic acid with gradual increase in the quantity of molybdate present is, on the whole, similar to that previously described. The first minimum occurs very near the same position as before, but seems to have a slightly less negative value, whilst the first maximum has a slightly higher value. A greater difference is to be observed in the second minimum which, for this solution, has a positive instead of a negative value. There is no definite indication, however, of a second maximum although the quantity of molybdate to malic acid was more than twice as much as in the previous case.

We also examined a solution of greater concentration as regards malic acid, and its behaviour is also shown in Fig. 3. The curve obtained is, on the whole, very similar to the first one described, and, in general, it may perhaps be said that increase in concentration of the malic acid compresses the whole concentration curve towards the left of the diagram, increased dilution having the opposite effect.

pounds of sodium molybdate and malic acid, we examined for comparison a solid compound obtained by dissolving 9 g. of malic acid and 8·1 g. of sodium molybdate in a small quantity of water, and then adding warm alcohol until a slight turbidity was produced. On *standing, light crystals filled the liquid and were*

FIG. 3.

Molecules $Na_2MoO_4,2H_2O$ *to* 1 *molecule* $C_4H_6O_5$.



filtered off, $[\alpha]_{5790}^{17^\circ}$ −48·55 ($c = 2·5$). On recrystallisation from aqueous alcohol, the rotation rose to −50·45° and remained constant on further recrystallisation, but analytical results agreed only approximately with the formula $2C_4H_6O_5,Na_2MoO_4$. A rough estimate of the change of rotation with concentration indicated that the specific rotation decreases on dilution.

Attempts were made to find an organic solvent for this compound,

but without success. The rotation was therefore observed in aqueous solution for six colours of light at different temperatures. The temperature-rotation curves showed no very characteristic peculiarity; the rotation increased in much the same way as for solutions in the neighbourhood of *A*, Fig. 1.

We thought it worth while also to ascertain whether, on mixing solutions of malic acid and of sodium molybdate, any gradual change of rotation with lapse of time—any lag—could be observed. In our first experiment, the two separate solutions were kept at room temperature for a considerable time, then mixed and immediately placed in the polarimeter. The rotation showed quite a considerable and steady change during about ½ hour. We found, however, that this was, in fact, a temperature effect. On mixing the two solutions there is a rise of temperature—which, of course, may indicate the formation of some compound—and, as the solution cooled, its rotation changed, in the manner of one of the curves in Fig. 2. If, after mixing, the solutions were quickly cooled to the original temperature by immersing the containing flask in water, no lag could be observed.

Experimental Data.

The colours of light used were the following and, to save space, will be denoted in the sequel by letters :

	r_1	r_2	y	g	b	v
λ	6716.	6234.	5790.	5461.	4916.	4359.

Data used for Fig. 1.

(*M* = g. of malic acid per 100 c.c.; *S* = g. of sodium molybdate per 100 c.c.)

M.	*S*.	$[\alpha]_y^{17^\circ}$.	$[\alpha]_g^{17^\circ}$.	$[\alpha]_v^{17^\circ}$.
9·325	0·4785	− 8·05°	− 9·40°	− 14·40°
9·307	4·00	− 53·0	− 61·4	−115·2
9·305	6·03	− 80·7	− 93·5	−176·8
9·323	7·99	− 90·72	−105·4	−202·1
9·322	8·41	− 86·44	−100·4	−191·9
9·325	9·07	− 71·45	− 82·44	−154·8
9·322	10·04	− 39·83	− 45·86	− 84·96
9·325	10·59	− 22·52	− 26·61	− 46·45
9·322	12·00	+ 23·41	+ 27·29	+ 58·39
9·322	14·07	+ 90·57	+105·4	+213·1
9·322	16·28	+154·5	+180·6	+360·8
9·322	16·51	+156·6	+183·1	+366·7
9·322	18·05	+141·8	+166·5	+332·9
9·322	20·00	+ 78·59	+ 92·82	+188·4
9·307	22·00	+ 17·45	+ 21·10	+ 47·00
9·307	24·00	− 5·40	− 5·60	− 6·70
9·325	26·22	− 10·70	− 12·10	− 19·85
9·285	28·91	− 16·01	− 18·40	− 34·38
9·325	33·61	− 9·10	− 9·70	− 19·80
9·307	35·77	+ 6·20	+ 7·00	+ 10·40
9·322	53·55	+ 69·92	+ 81·27	+147·9

Solution 1.

Malic acid, $c = 9{\cdot}307$, $p = 7{\cdot}849$; sodium molybdate, $c = 22{\cdot}00$.

t.	d.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·1932	+ 5·21°	+ 6·56°	+ 8·54°	+10·81°	+15·55°	+26·43°
16	1·1871	11·47	13·75	17·37	20·79	29·71	45·81
27	1·1821	14·62	17·92	22·43	26·74	37·38	57·79
35·8	1·1775	17·11	21·57	26·58	31·65	44·36	67·76

Solution 2.

Malic acid, $c = 9{\cdot}307$, $p = 7{\cdot}775$; sodium molybdate, $c = 24{\cdot}00$.

t.	d.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·2127	−9·08°	−10·61°	−12·10°	−13·59°	−16·44°	−23·47°
11	1·2075	−5·92	− 7·02	− 8·32	− 9·19	−10·38	−13·98
16	1·2050	−4·60	− 5·14	− 6·00	− 6·27	− 6·80	− 7·60
19·5	1·2032	−4·01	− 4·28	− 4·31	− 4·28	− 3·94	− 4·01
22·5	1·2018	−2·94	− 2·74	− 2·54	− 2·34	− 1·81	− 0·69
27·5	1·199	−1·21	− 0·47	+ 0·13	+ 0·94	+ 2·48	+ 6·17
37·5	1·1935	+3·06	+ 3·74	+ 5·79	+ 7·21	+11·15	+19·03

Solution 3.

Malic acid, $c = 9{\cdot}325$, $p = 7{\cdot}711$; sodium molybdate, $c = 26{\cdot}22$.

t.	d.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·221	−10·83°	−12·74°	−14·60°	−16·79°	−21·94°	−31·10°
13	1·2148	− 9·61	−10·48	−11·94	−13·51	−16·88	−23·69
35	1·2034	− 3·17	− 3·23	− 3·03	− 2·96	− 2·29	− 1·35
44·8	1·1976	± 0	+ 0·41	+ 1·49	+ 2·40	+ 4·74	+ 9·95
55·5	1·1910	+ 3·69	+ 4·70	+ 6·74	+ 8·54	+13·20	+21·64

Solution 4.

Malic acid, $c = 9{\cdot}285$, $p = 7{\cdot}566$; sodium molybdate, $c = 28{\cdot}91$.

t.	d.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·2384	− 9·81°	−11·15°	−12·94°	−14·94°	−19·88°	−29·28°
11	1·2335	—	—	−15·77	−18·22	—	−34·19
17	1·2306	−12·09	−13·97	−16·01	−18·40	−24·24	−34·38
37·5	1·2195	− 8·81	−10·03	−11·72	−13·18	−15·92	−22·10
49·5	1·2123	− 5·66	− 6·13	− 6·95	− 7·53	− 8·59	−10·22
58·5	1·2065	− 2·64	− 2·60	− 2·53	− 2·40	− 1·64	+ 0·75

Solution 5.

Malic acid, $c = 9{\cdot}325$, $p = 7{\cdot}455$; sodium molybdate, $c = 33{\cdot}61$.

t.	d.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·2660	+2·10°	+ 2·32°	+ 4·07°	+ 3·84°	+ 4·37°	+ 5·63°
19	1·2562	−7·27	− 8·48	− 9·94	−10·41	−14·42	−21·22
30	1·2502	−9·39	−11·23	−12·54	−14·35	−18·64	−27·13
40·4	1·2440	−9·84	−11·26	−12·27	−14·22	−18·53	−26·15
48·2	1·2390	−9·00	− 9·81	−11·44	−12·42	−16·17	−22·19

Solution 6.

Malic acid, $c = 9{\cdot}307$, $p = 7{\cdot}285$; sodium molybdate, $c = 35{\cdot}77$.

t.	d.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·2938	+18·37°	+21·48°	+26·19°	+30·04°	+38·46°	+52·18°
16	1·2854	+ 4·77	+ 5·81	+ 7·14	+ 8·28	+10·35	+12·75
20·5	1·2828	+ 1·94	+ 2·41	+ 3·38	+ 3·68	+ 4·95	+ 5·15
24·2	1·2806	+ 0·33	+ 0·54	+ 0·87	+ 0·94	+ 0·87	+ 0·60
25·5	1·2800	− 0·44	− 0·47	± 0·00	− 0·27	− 0·60	− 2·01
29·2	1·2778	− 1·95	− 2·15	− 2·35	− 2·89	− 3·83	− 7·42

Data used for Fig. 3.

(S = g. of sodium molybdate per 100 c.c.; n = mols. of $Na_2MoO_4,2H_2$(per mol. of $C_4H_6O_5$.)

Malic acid, c = 17·88.

Rotations (t = 17°, approx.).

S.	n.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_v$.
5·127	0·1588	− 36·13°	− 42·34°	− 78·64°
10·201	0·3159	− 70·81	− 82·55	−156·9
15·24	0·4719	− 98·49	−114·5	−218·5
20·13	0·6233	− 38·48	− 50·28	− 82·77
21·899	0·6780	− 3·84	− 4·05	—
22·51	0·6971	+ 6·33	+ 7·38	+ 18·79
24·966	0·7732	+ 41·61	+ 47·48	+ 97·99
30·37	0·9404	+132·2	+154·8	+310·9
32·01	0·991	+153·6	+179·3	+359·6
32·23	0·998	+155·4	+182·3	—
32·35	1·00	+157·4	+184·5	+370·2
35·00	1·084	+121·5	+142·3	+359·6
40·15	1·243	+ 38·31	+ 45·58	+ 96·25
42·71	1·323	+ 13·02	+ 15·45	—
45·06	1·395	− 11·07	− 12·64	− 20·75
50·04	1·550	− 17·00	− 19·96	—
55·10	1·706	− 6·77	− 7·83	− 17·28
60·78	1·882	+ 18·46	+ 21·08	—

Malic acid, c = 2·55.

Rotations (t = 17°, approx.).

S.	n.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_v$.
0·96	0·2084	− 47·45	− 54·13	−105·9
2·017	0·438	− 90·59	−106·3	−199·6
2·395	0·5201	− 72·16	− 87·46	−166·7
2·60	0·5646	− 54·91	− 64·71	−121·6
4·033	0·8758	+114·5	+132·5	+264·3
4·348	0·9443	+143·5	+166·3	+334·1
4·612	1·0002	+156·9	+183·1	+364·8
5·03	1·092	+164·7	+193·7	+382·3
5·437	1·181	+160·1	+187·5	+370·2
5·922	*1·286*	*+145·5*	*+171·4*	*+339·2*
7·01	1·523	+ 97·27	+115·3	+230·2
8·093	1·758	+ 57·27	+ 67·45	+137·4
9·433	2·048	+ 28·63	+ 33·73	+ 69·42
9·905	2·151	+ 23·14	+ 27·06	+ 54·90
10·76	2·336	+ 16·87	+ 19·81	+ 41·97
11·40	2·476	+ 14·51	+ 15·69	+ 34·90
12·15	2·638	+ 12·94	+ 14·51	+ 28·23
12·975	2·818	+ 12·55	+ 14·51	+ 29·81
13·404	2·911	+ 12·55	+ 15·30	+ 29·81
15·018	3·262	+ 14·90	+ 17·65	+ 32·95
16·404	3·562	+ 19·22	+ 22·75	+ 40·00
19·146	4·158	+ 27·06	+ 32·16	+ 60·39
25·11	5·464	+ 48·23	+ 56·48	+103·1
29·732	6·457	+ 64·71	+ 72·56	+135·7
34·97	7·595	+ 81·96	+ 95·3	+177·6
39·81	8·646	+ 94·52	+108·6	+203·9

Rotations of sodium molybdomalate, $2C_4H_6O_5,Na_2MoO_4$, in water (p = 23·37).

t.	d.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_v$.
0°	1·1540	−35·34°	−41·65°	−49·97°	−58·38°	−112·9°
16	1·1484	37·22	44·18	52·43	61·53	116·7
25·5	1·1444	38·35	45·53	54·29	63·36	121·3
37	1·1390	39·03	46·29	55·35	64·58	122·4
45·5	1·1345	39·42	46·85	56·04	64·88	122·9

For this solution the rotation for blue could not be read.

Our thanks are due to the Carnegie Trustees for the Universities of Scotland for a grant which defrayed part of the cost of this investigation.

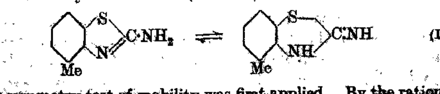
UNIVERSITY OF GLASGOW. [*Received, July 14th,* 1928.]

CCCXCVI.—*Aminobenzthiazoles. Part X. The Mobility of the* 1-*Amino*-3-*methylbenzthiazole System.*

By ROBERT FERGUS HUNTER and ERIC ROFE STYLES.

IN Part III (J., 1926, 1385) it was shown that rational syntheses of 1-aminobenzthiazole and of 1-imino-1 : 2-dihydrobenzthiazole led to a single individual which gave almost quantitatively the 1-imino-2-alkyl-1 : 2-dihydro-derivative on alkylation and 1-acetamido-benzthiazole on acetylation. On the basis of those experiments, the mobility of the symmetrical triad system in 1-aminobenzthiazole was regarded as being established.

That experimental evidence, however, is somewhat slender to carry the superstructure of the theories which have been suggested in Parts V to IX. Moreover, the criticism has still to be met, that the isolation of the second alkyl derivative of 1-aminobenzthiazole was left doubtful; for Pyman (J., 1923, **123**, 367, 3359) has shown that mobile open-chain amidines invariably react in two tautomeric forms on methylation. It was therefore decided to establish the mobility of a typical substituted 1-aminobenzthiazole by means of evidence of the symmetry type (Ingold and Piggott, J., 1922, **121**, 2381) and of the substitution type (*idem*, J., 1923, **123**, 1470) about which there could be no question. The example chosen was 1-amino-3-methylbenzthiazole (I ⇌ II).

(I.)  (II.)

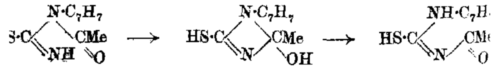
The symmetry test of mobility was first applied. By the rational syntheses mentioned below, 1-*acetamido*-3-*methylbenzthiazole* (III) and

imino-2-acetyl-3-methyl-1 : 2-dihydrobenzthiazole (IV) were prepared ıd these yielded the same tautomeric base (I ⇌ II) on hydrolysis oreover, (III) was obtained in almost quantitative yield by direct etylation of 1-amino-3-methylbenzthiazole with acetic anhydride

II.) $C_6H_3Me<^{S}_{N}\gg C\cdot NHAc$ $C_6H_3Me<^{S}_{NAc}>C:NH$ (IV.)

Under the usual conditions, bromination of stable acetyl-*o*-tolyl- *iocarbamide*, $C_7H_7\cdot NH\cdot CS\cdot NHAc$ (*Hugershoff*, *Ber.*, 1899, **32**, 49; Wheeler, *Amer. Chem. J.*, 1902, **27**, 270) readily produced a *rabromide* of 1-acetamido-3-methylbenzthiazole, which gave the pected base (III) on reduction with sulphurous acid. Bromin- ion of labile acetyl-*o*-tolylthiocarbamide, $C_7H_7\cdot NAc\cdot CS\cdot NH_2$, der carefully controlled conditions led to the production of a *bromide* (compare Hunter, J., 1926, 1395), which gave the iso- eric iminoacetyldihydrobenzthiazole (IV) on reduction.

When the temperature was allowed to rise, or when a considerable cess of bromine was employed, during the bromination of *labile* etyl-*o*-tolylthiocarbamide, the product consisted, not of the pected iminoacetyldihydrobenzthiazole tribromide, but of the trabromo-addition compound obtainable by bromination of the meric *stable* acetyl-*o*-tolylthiocarbamide. This result was evi- ntly due to conversion of the labile into the stable acetylthio- rbamide under the influence of bromine, similar to the isomer ıtion which these compounds are known to undergo under the fluence of alkalis (Wheeler, *loc. cit.*), followed by thiazole ring rmation in the usual way (Hunter and Soyka, J., 1926, 2958) his curious isomerisation may be explained by assuming th rmation of an intermediate, unstable, four-membered, heterocycli mpound of the 1 : 3-dimethindiazine type obtained by Ingold ıd Piggott (J., 1922, **121**, 2797) by the additive union of suitabl omethines (compare also Ingold and Piggott, J., 1923, **123**, 2746 gold, J., 1925, **127**, 1141) :



The substitution test completely supported the symmetry test mobility (compare Ingold and Piggott, J., 1923, **123**, 1471), for ethylation of the single individual (I ⇌ II) gave rise to a xture of 1-*methylamino-3-methylbenzthiazole* (V) and 1-*imino-* . 3-*dimethyl*-1 : 2-*dihydrobenzthiazole* (VI) containing about 1% of the former. (V and VI are III and IV, respectively, with Me in place of Ac.)

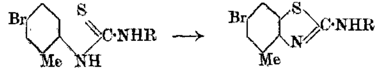
The addition of methyl iodide to mobile and to static amidines Burtles and Pyman, J., 1923, **123**, 362; Pyman, *ibid.*, pp. 367, 3359) appears to indicate that the first action of methyl iodide on he former is one of direct addition to the double-bonded nitrogen toms of both phases of the tautomeric system, with the production f isomeric methiodides which pass into the hydriodides of the nethyl derivatives derived from the isomeric forms of the mobile ndividual:

–[H]N·C:N ⟶ –[H]N·C:N(MeI) ⟶ –N:C·N[H](MeI) ⟶ –N:C·NMe(HI)
–N:C·N[H] + –(MeI)N:C·N[H] + –(MeI)N[H]·C:N + –(HI)NMe·C:N

The suggestion (Hunter, J., 1926, 1389) that iminomethyldi-ydrobenzthiazole is obtained from the iminodihydro-phase by irect replacement of the mobile hydrogen atom (compare von 'echmann, *Ber.*, 1897, **30**, 481; Lander, J., 1903, **83**, 320; Cohen nd Marshall, J., 1910, **97**, 329) must therefore be modified (compare 'oung and Crookes, J., 1906, **89**, 59; Tschitschibabin and Konowa-owa, *Ber.*, 1921, **54**, 814). The methylation of semi-cyclic amidines 1 which one of the nitrogen atoms of the triad system is part of n aromatic heterocyclic nucleus, as in aminothiazoles and α-amino-yridines, is evidently dependent on the aromatic conjugation of ie system, a topic which will be more fully discussed in a future aper.

The bromo-addition compounds of 1-amino-3-methylbenzthiazole nd its derivatives were reduced by hydriodic acid in acetic acid, ut owing to the readiness with which they changed into bromo-ibstitution compounds it was impossible to estimate the labile romine iodometrically.

The bromo-substitution compounds were shown to be 5-*bromo*-1-*'kylamino-3-methylbenzthiazoles* (VIII) by rational syntheses of the amino-, 1-*n*-propylamino-, and 1-*n*-heptylamino-compounds from ie corresponding *p*-bromo-*o*-tolylthiocarbamides (VII).

VII.)  (VIII.)

EXPERIMENTAL.

'automeric substances are named on the basis of the amino-formulæ.)

Synthesis of 1-*Amino-3-methylbenzthiazole from* 1-*Imino-2-acetyl-methyl*-1 : 2-*dihydrobenzthiazole* (IV).—A solution of 5·5 g. of bile acetyl-*o*-tolylthiocarbamide (m. p. 140°) in 50 c.c. of chloro-

form was gradually treated at 0° with bromine (2·5 c.c.) in chloroform (7 c.c.). The liquid was rapidly filtered and kept for 10—15 minutes at about 0° in a vacuum. The yellow needles of the *tribromide* produced, m. p. 173° (decomp.), after drying in a vacuum (Found: Br, 53·5. $C_{10}H_{10}ON_2Br_2S,HBr$ requires Br, 53·8%), were suspended in sulphurous acid and treated with sulphur dioxide and thereafter with ammonia (*d* 0·880). The 1-*imino*-2-*acetyl*-3-*methyl*-1 : 2-*dihydrobenzthiazole* obtained crystallised from absolute methyl alcohol in pale yellow prisms, m. p. 170° (Found: N, 13·4; S, 15·5. $C_{10}H_{10}ON_2S$ requires N, 13·6; S, 15·5%). It was refluxed with 25% hydrochloric acid for 24 hours, and the cooled solution neutralised with ammonia. The 1-amino-3-methylbenzthiazole produced crystallised from alcohol in small white plates which, alone or mixed with a genuine specimen, melted at 136° (Found: S, 19·7. Calc.: S, 19·5%).

Synthesis from 1-*Acetamido*-3-*methylbenzthiazole*.—A suspension of stable acetyl-*o*-tolylthiocarbamide (m. p. 187°) (2 g.) in chloroform (15 c.c.) was slowly treated with bromine (2 c.c. in 3 c.c. of chloroform), and the resulting solution refluxed for 10 minutes. On cooling, a *tetrabromide* separated in orange needles, which were dried in a vacuum; m. p. 140° (decomp.) (Found: Br, 61·1. $C_{10}H_{10}ON_2Br_4S$ requires Br, 60·8%). 1-*Acetamido*-3-*methylbenzthiazole*, obtained from this by reduction with sulphurous acid, separated from ethyl acetate in lustrous needles, m. p. 258° (Found: N, 13·8; S, 15·7. $C_{10}H_{10}ON_2S$ requires N, 13·6; S, 15·5%); it was identical with the acetyl derivative obtained by boiling a solution of 1-amino-3-methylbenzthiazole in acetic anhydride for a few minutes. On hydrolysis with 25% hydrochloric acid, 1-amino-3-methylbenzthiazole was obtained and identified in the usual way.

Bromination of 1-acetamido-3-methylbenzthiazole (0·5 g. in 25 c.c. of chloroform; 0·6 c.c. of bromine) yielded an unstable *hexabromide*, which crystallised in glistening orange plates, m. p. 255—258° (decomp.; loss of bromine at about 130°) (Found: Br, 69·8. $C_{10}H_{10}ON_2Br_6S$ requires Br, 70·0%).

Synthesis from 1-*Amino*-3-*methylbenzthiazole Dibromide Hydrobromide*.—A suspension of 2 g. of *o*-tolylthiocarbamide in 16 c.c. of chloroform was treated with bromine (2 c.c. in 3 c.c. of chloroform); the thiocarbamide dissolved and a yellow precipitate separated and redissolved with evolution of heat and hydrogen bromide, the solution boiling spontaneously. After a few minutes' refluxing, the *dibromide hydrobromide* crystallised in large, lustrous, orange-yellow plates, m. p. 129° (decomp. with efferv.) [Found: Br, 59·0; Br (labile), 35·0. $C_8H_8N_2Br_2S,HBr$ requires Br, 59·3;

amount of the bromo-addition compound passing into 5-bromo-1-amino-3-methylbenzthiazole hydrobromide, a change which has been observed by Prof. R. W. West and his collaborators (private communication) in the case of perbromides of aromatic bases having a free *para* position (compare also Fries, *Annalen*, 1906, **346**, 128). The bromide dissolved in 80% alcohol, from which 5-*bromo*-1-*amino*-3-*methylbenzthiazole hydrobromide* crystallised in small white needles, m. p. 280—290° (with charring) (Found: Br, 49·1. $C_8H_7N_2BrS,HBr$ requires Br, 49·4%). Treatment of the bromide with sulphurous acid and subsequent basification, however, gave a quantitative yield of 1-amino-3-methylbenzthiazole, m. p. 136°.

When prepared as above, in large crystals, the dibromide hydrobromide can be preserved in a sealed vessel for more than a year. Small crystals (having the same crystalline structure and m. p. as before), obtained by alteration in the conditions of concentration and separation, are sensitive to moisture; one specimen, on exposure to the laboratory atmosphere for 30 hours, was completely converted into 1-*amino*-3-*methylbenzthiazole hydrobromide* (m. p. 220°), identical with the hydrobromide prepared by concentrating a solution of 1-amino-3-methylbenzthiazole in 20% hydrobromic acid; this crystallised in small needles, m. p. 220—222° (Found: Br, 32·0. $C_8H_8N_2S,HBr$ requires Br, 32·6%).

1-*Amino*-3-*methylbenzthiazole Tetrabromide*.—When a solution of 0·6 g. of 1-amino-3-methylbenzthiazole in 10 c.c. of chloroform was gradually treated with a solution of bromine (0·4 c.c. in 5 c.c. of chloroform) a *tetrabromide* was obtained in yellowish-brown prisms, m. p. 302° (loss of colour at 130—140°) (Found: Br, 65·9. $C_8H_8N_2Br_4S$ requires Br, 66·1%).

Methylation of 1-*Amino*-3-*methylbenzthiazole and the Isolation of* 1-*Methylamino*-3-*methylbenzthiazole and of* 1-*Imino*-2 : 3-*dimethyl*-1 : 2-*dihydrobenzthiazole*.—A mixture of 1-amino-3-methylbenzthiazole (3·5 g.) and methyl iodide (2·5 c.c.) was heated at 100° for 24 hours; the product was basified with ammonia and extracted with ether. The clear oil obtained after removal of the ether solidified on keeping (sometimes with considerable difficulty) and was fractionally crystallised from methyl alcohol. The first crop of crystals (about 0·02 g.) had m. p. 126°, which rose to 128° on recrystallisation and was unaltered by admixture with a genuine specimen of 1-methylamino-3-methylbenzthiazole prepared from o-tolylmethylthiocarbamide. (A mixture of 1-methylamino-3-methylbenzthiazole and 1-amino-3-methylbenzthiazole melted at 103—105° after softening at about 100°.) The more soluble crop

1 : 2-dihydrobenzthiazole then separated. This product had m. 83—84°, and m. p. 84—85° when mixed with a genuine specim of 1-imino-2 : 3-dimethyl-1 : 2-dihydrobenzthiazole prepared fro *as-o*-tolylmethylthiocarbamide; on recrystallisation the m. rose to 85—86°. The crude iminomethyl base was acetylated wi acetic anhydride, and the product fractionally crystallised fro alcohol; the bulk of the acetyl derivative consisted of the 1-ace imido-compound, which had m. p. 143°, and m. p. 145° when mix with a genuine specimen of 1-acetimido-2 : 3-dimethyl-1 : 2-d hydrobenzthiazole. The mother-liquor from the acetylatio however, yielded a high-melting fraction, which, after recryst lisation, had m. p. 258° alone and when mixed with 1-acetamid 3-methylbenzthiazole.

Synthesis of 1-Methylamino-3-methylbenzthiazole and of 1-Imin 2 : 3-dimethyl-1 : 2-dihydrobenzthiazole from the Corresponding Tol methylthiocarbamides.—*o*-Tolylthiocarbimide was conveniently pr pared in 80—90% yield (b. p. 238—240°/760 mm.) by refluxi quantities of 50 g. of *s*-di-*o*-tolylthiocarbamide with acetic anhydri (60 c.c.) for 10 minutes, being isolated by distillation in stea *o*-Tolylthiocarbamide separated from 50% alcohol in glisteni white needles, m. p. 160° (Dyson and George, *J.*, *1924*, **125**, 170 recorded m. p. 156°).

s-o-*Tolylmethylthiocarbamide*, prepared by treating 5 g. of *o*-tol thiocarbimide in 20 c.c. of absolute alcohol with a 30% excess 33% methylamine in the same solvent, crystallised in glisteni prisms, m. p. 161° (Found: S, 17·8. $C_9H_{12}N_2S$ requires S, 17·8%

Bromination. A suspension of 2 g. of *s*-*o*-tolylmethylthiocar amide in 10 c.c. of chloroform was treated with bromine (2 c.c. 3 c.c. of chloroform) and the liquid was refluxed vigorously f 10 minutes and then concentrated in a vacuum at laboratory te perature; a *tetrabromide* crystallised in glistening red needl m. p. 75° (decomp.) (Found: Br, 64·4. $C_9H_{10}N_2Br_4S$ requir Br, 64·2%). This compound was extremely sensitive to moist a and became yellow with loss of bromine on being exposed to t laboratory atmosphere for a few minutes.

When the bromination was carried out as above, but instead being vigorously boiled, the solution was gently warmed on t steam-bath, a *tribromide* was obtained on concentration in a vacuu which was probably the dibromide of a hydrobromide analogous the compound obtained from *o*-tolylthiocarbamide itself; formed glistening yellow prisms, m. p. 113° (Found: Br, 57· $C_9H_{10}N_2Br_2S,HBr$ requires Br, 57·3%). Attempts to determi its molecular weight in boiling chloroform (previously dried) we

bromine; on prolonged boiling in chloroform, hydrogen bromide also was liberated.

Both the tetrabromide and the tribromide dissolved in sulphurous acid, and on basification with ammonia, 1-*methylamino*-3-*methylbenzthiazole* separated, which crystallised from alcohol in lustrous needles, m. p. 130° (Found : N, 15·9; S, 18·2. $C_9H_{10}N_2S$ requires N, 15·7; S, 18·0%). The *acetyl* derivative, prepared as in the case of the isomeric iminodihydro-derivative, crystallised from alcohol–ethyl acetate in white needles, m. p. 133° (Found: S, 14·6. $C_{11}H_{12}ON_2S$ requires S, 14·5%).

as-o-*Tolylmethylthiocarbamide*.—Addition of methyl-*o*-toluidine in chloroform to thiocarbonyl chloride in water (compare Dyson and George, *loc. cit.*) gave a thiocarbamyl chloride which yielded uncrystallisable oils on treatment with ammonia. The thiocarbamide was therefore prepared by way of the thiocyanate. A solution of 10 g. of methyl-*o*-toluidine hydrochloride and 7 g. of potassium thiocyanate in 50 c.c. of water was heated for 3 hours on a steam-bath and then extracted with chloroform. The gum obtained by evaporation of the chloroform crystallised from methyl alcohol in small, white needles (3·5 g.), m. p. 107—108° (Found : S, 17·6%).

Bromination. The solution obtained from 1 g. of the thiocarbamide, 7 c.c. of chloroform, and 1 c.c. of bromine was refluxed for 3 minutes and then concentrated under reduced pressure at laboratory temperature. The orange bromo-addition compound obtained was dissolved in sulphurous acid and the filtered solution was basified and extracted with chloroform. The gum obtained by evaporation of the chloroform was dissolved in 80—90% methyl alcohol, and the solution concentrated at 16°/20 mm.; 1-*imino*-1 : 3-*dimethyl*-1 : 2-*dihydrobenzthiazole* crystallised in small white plates, m. p. 86° (Found : S, 18·1%). The *acetyl* derivative separated from alcohol in glistening plates, m. p. 147° (Found : S, 14·7%).

5-*Bromo*-1-*amino*-3-*methylbenzthiazole*.—A suspension of 0·9 g. of p-bromo-*o*-tolylthiocarbamide (m. p. 194°. Dyson and George, J., 1924, **125**, 1706, give 186°) in chloroform (10 c.c.) was treated with bromine (1·1 c.c. in 1 c.c. of chloroform), and the solution refluxed for 10 minutes; a *dibromide hydrobromide* crystallised in orange, glistening prisms, which turned white at 130—140° but were unmelted at 250° (Found: Br, 66·3. $C_8H_7N_2Br_3S,HBr$ requires Br, 66·1%). On treatment with sulphurous acid and ammonia, it yielded 5-bromo-1-amino-3-methylbenzthiazole, which crystallised from alcohol in needles, m. p. 212°, and was identical with the base liberated from the hydrobromide obtained by the action of alcohol

s-o-*Tolyl*-n-*propylthiocarbamide* was prepared by warming solution of *o*-tolylthiocarbimide in alcohol with 30% excess c *n*-propylamine. It separated from the solution after concentratio and crystallised from alcohol in colourless prisms, m. p. 66° (Found S, 15·5. $C_{11}H_{16}N_2S$ requires S, 15·4%).

1-n-*Propylamino-3-methylbenzthiazole Tetrabromide*.—A solutio of 2 g. of *s*-*o*-tolyl-*n*-propylthiocarbamide in 10 c.c. of chlorofor was treated with bromine (2 c.c. in 3 c.c. of chloroform), and th liquid vigorously refluxed for 10 minutes. On concentration in vacuum the *tetrabromide* crystallised in brilliant red needles, m. p 71° (efferv. at 130°) (Found: Br, 60·6. $C_{11}H_{14}N_2Br_4S$ require Br, 60·8%). On treatment with sulphurous acid followed b ammonia the *base* was obtained; it crystallised from methyl alcoh in colourless needles, m. p. 62° (Found: S, 15·7. $C_{11}H_{14}N_2$ requires S, 15·5%). The *hydrobromide* crystallised from eth acetate in prisms, m. p. 179° (decomp. after previous sinterin (Found: N, 10·0. $C_{11}H_{14}N_2S$,HBr requires N, 9·8%).

The *acetyl* derivative formed colourless prisms, m. p. 61° (Found S, 13·0. $C_{13}H_{16}ON_2S$ requires S, 12·9%).

When a solution of the tetrabromide in alcohol was diluted wit a small quantity of water and concentrated, the *hydrobromide* c the bromo-substitution derivative separated; this crystallised fro alcohol in tufts of fine white needles, m. p. 259° (Found: Br, 45· $C_{11}H_{13}N_2BrS$,HBr requires Br, 43·7%).

s-5-*Bromo*-o-*tolyl*-n-*propylthiocarbamide*, prepared from 5-bromo o-tolylthiocarbimide and *n*-propylamine, crystallised from meth alcohol in slender white needles, m. p. 79° (Found: S, 11·4 $C_{11}H_{15}N_2BrS$ requires S, 11·2%).

5-*Bromo*-1-n-*propylamino-3-methylbenzthiazole*.—A solution of 1 g of the bromotolylthiocarbamide in chloroform (10 c.c.) was reflux with 1·2 c.c. of bromine for 15 minutes, cooled, and concentrated i a vacuum; an ill-defined bromo-addition compound separate (m. p. about 140°), which was reduced with sulphurous acid in th usual way. On recrystallisation from methyl alcohol, 5-*bromo* 1-n-*propylamino-3-methylbenzthiazole* was obtained, m. p. 82°, whic was identical with the base (m. p. 82°) liberated from the last mentioned hydrobromide (Found: Br, 28·3. $C_{11}H_{13}N_2BrS$ require Br, 28·1%).

s-o-*Tolyl*-n-*heptylthiocarbamide* was prepared from *o*-tolylthio carbimide and *n*-heptylamine and obtained as a viscous oil whic gradually solidified in a vacuum. It crystallised from alcohol i

brominated as in the case of the propyl compound, an unstable *hexabromide* was obtained in orange-red needles, m. p. 53° (sintering at 45°) (Found: Br, 64·4. $C_{15}H_{22}N_2Br_6S$ requires Br, 64·7%).

1-n-*Heptylamino-3-methylbenzthiazole* crystallised with difficulty from dilute methyl alcohol in white prisms, m. p. 57° (Found: S, 12·4. $C_{15}H_{22}N_2S$ requires S, 12·2%). The *acetyl* derivative formed stellate aggregates of needles, m. p. 73° (Found: S, 10·6. $C_{17}H_{24}ON_2S$ requires S, 10·5%).

The hexabromide dissolved in aqueous alcohol, giving the *hydrobromide* of the bromo-substitution derivative, which crystallised from alcohol in small, white plates, m. p. 220° (Found: Br, 37·6. $C_{15}H_{21}N_2BrS,HBr$ requires Br, 37·9%).

s-5-*Bromo*-o-*tolyl*-n-*heptylthiocarbamide* separated from dilute methyl alcohol in small white needles, m. p. 71° (Found: S, 10·1. $C_{15}H_{23}N_2BrS$ requires S, 9·3%).

5-*Bromo*-1-n-*heptylamino*-3-*methylbenzthiazole*.—The bromo-addition compound obtained from the bromotolylthiocarbamide was reduced and the 5-*bromo-base* produced was crystallised from dilute methyl alcohol; it had m. p. 75° alone and when mixed with the base (m. p. 75°) liberated from the preceding hydrobromide (Found: N, 8·6; Br, 23·7. $C_{15}H_{21}N_2BrS$ requires N, 8·2; Br, 23·5%).

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CCCXCVII.—*The Interaction of Acids and Neutral Salts with Stannic Oxide and its Relation to Electrical Charge.*

By BHUPENDRA NATH GHOSH.

IN a previous paper (J., 1926, 2605) the inadequacy of the chemical theory to account for the development of an acid reaction when hydrated oxides of manganese are treated with solutions of neutral salts has been pointed out. It has also been shown how Mu

According to this theory, the liberation of hydrogen ions is to be attributed to their displacement from the double layer by the kations in solution. Like the oxides of manganese, hydrated stannic oxide is also known to liberate acids when brought in contact with solutions of neutral salts. As early as 1812, from his investigations on the properties of stannic oxide prepared by various methods, Berzelius concluded that the substance is acidic in nature and exists in two forms—the α- and β-stannic acids. There is, however, considerable controversy over the actual existence of these different forms. The so-called α-acid may be prepared by the hydrolysis of stannic chloride or sulphate solution, or by the action of alkalis on them in the cold; the β-acid may be obtained by the action of concentrated nitric acid on metallic tin. The existence of definite hydrates of the two acids has also been reported by different investigators (compare Weiser, *J. Physical Chem.*, 1922, **26**, 654). Van Bemmelen ("Die Absorption," 1910, 59, 66) studied the dehydration of stannic oxide prepared by different methods, but his results do not confirm the existence of any definite hydrate of either acid. Mecklenburg (*Z. anorg. Chem.*, 1912, **74**, 207) measured the adsorption of phosphoric acid by stannic oxide prepared at different temperatures, and showed that by suitable variation of temperature it is possible to obtain samples having all grades of properties intermediate between the α- and the β-acid. Hence he concluded that both acids are colloidal in nature and that the difference in their properties is mainly due to the difference in the size of their particles, the α-acid being the more finely divided. Recently the question of the formation of stable hydrates of stannic oxides has again been raised by Willstätter and his collaborators (*Ber.*, 1924, **57**, 63). Their views have, however, been adversely criticised by Posnjak (*J. Physical Chem.*, 1926, **30**, 1073), who investigated the *X*-ray spectra of both the α- and the β-oxide. His results seem strongly to support the views of Mecklenburg, for the lines from the α-acid are wider than those from the β-acid, showing that the former possesses particles of finer size than the latter. In view of these controversies, the interaction of the α- and β-stannic oxides with electrolytes was investigated.

EXPERIMENTAL.

β-Stannic acid, prepared by the action of concentrated nitric acid on pure metallic tin, was washed by decantation with boiling water, and then with boiling conductivity water. The final washing was done under suction on a Buchner funnel until the p_H of

The α-acid was obtained by adding dilute ammonia to a solution of stannic chloride at 5°. The precipitate was washed several times with cold water, then with dilute nitric acid to remove the last traces of ammonia, and finally with conductivity water until the p_H of water in contact with it was 6·0.

Estimation of the Total Amount of Hydrogen Ions replaceable by the Kation of a Neutral Salt.—The α- and the β-oxide are known to form alkali salts of the form R_2O,SnO_2 and $R_2O,5SnO_2$, respectively (compare J. N. Friend, "Text Book of Inorganic Chemistry," Vol. V, p. 533). Since the samples that we are dealing with liberate hydrogen ions in contact with neutral salts, the question naturally arises as to what will be the final composition of the substances when all the hydrogen ions are removed by washing with the solution of a salt such as barium chloride. A definite weight of hydrated stannic oxide was therefore shaken with a known volume of saturated barium chloride solution (p_H 6·6) in a Pyrex-glass bottle for 15 minutes. After 24 hours as much as possible of the clear upper liquid was withdrawn and its p_H determined by either the *E.M.F.* or the indicator method. A measured volume of fresh barium chloride solution was added and the whole process repeated many times. With the progress of washing the p_H of the solution rose continuously as shown by the following data for 3 g. of the β-oxide (water content, 55%):

Vol. of solution added, c.c.	Vol. of solution withdrawn, c.c.	Final p_H of solution.
200	160	3·1
200	160	3·2
200	200	3·3

Towards the end, however, the hydrogen-ion concentration changed very slowly, and a small quantity of 0·2*N*-barium hydroxide was therefore added to bring the p_H of the solution to 6·6. In this way it is found that for every 6·6 g.-mols. of the β-oxide there is 1 g.-atom of replaceable hydrogen.

The total amount of replaceable hydrogen ions was also estimated by a different method. To a large volume of saturated barium chloride solution in contact with stannic oxide barium hydroxide solution was added in small quantities at a time, each addition being followed by a vigorous shaking. Here also, with both the α- and the β-oxide, the p_H of the solution was found to increase regularly with increasing amounts of alkali added. The addition of alkali was continued until the p_H of the barium chloride solution had risen to about 6·7. By this method it is found that every

In the case of the α-oxide, it is found that for every 4·9 g.-mols. of SnO_2 there is 1 g.-ion of replaceable hydrogen. This shows that for every molecule of SnO_2 the α-oxide contains more replaceable hydrogen ions than the β-oxide. In both cases, however, the stoicheiometric ratio $SnO_2 : H$ is fractional. Further, the increase in p_H observed with repeated washing by barium chloride solution or with successive additions of small quantities of alkali cannot be satisfactorily explained from the chemical point of view of insoluble salt formation. This has been discussed in detail in the previous paper (*loc. cit.*).

Electrical Adsorbability of the Kations and their Capacity to liberate Hydrogen Ions.—20 G. of the β-oxide were shaken with 200 c.c. of the electrolyte solution as before. After 24 hours the clear supernatant solution was withdrawn, and its p_H measured by the *E.M.F.* method. In this way the concentration of hydrogen ions liberated by different salts at the same gram-molecular concentration was determined. The electrical charge of the substance was measured by the electro-endosmotic method. The arrangement used is an improvement of that previously described by the author (*loc. cit.*). The electro-endosmotic flow of a liquid through a porous diaphragm depends, among other factors, directly on the potential across the latter. In the present arrangement a definite potential as indicated by a voltmeter was applied between the electrodes, and could be maintained constant within ± 1 volt by means of an adjustable resistance. The potential across the diaphragm was determined in the following way. The total resistance, consisting of that of the diaphragm and the electrolyte, was measured by the conductivity method. The electrodes were then lowered so as just to touch the ends of the diaphragm and the resistance was measured again. If T and D be the total and the diaphragm resistances respectively, then the potential across the diaphragm is given by the expression DV/T, where V is the potential indicated by the voltmeter when the electrodes were in their original position (*i.e.* when the resistance between them was T). In order that the potential across the diaphragm should remain constant during the electro-endosmotic experiment it is necessary that D/T should remain constant: the maximum variation in this ratio before and after the experiment was always within 3%, and the mean was used in calculating the potential. The value of D/T was, however found to increase with increasing concentration of the electrolytes even when the other factors, such as the length of the diaphragm

Concentration of electrolyte.	Values of D/T for KCl.	LiCl.	NaCl.
0·0002N	0·53	0·54	0·53
0·001	0·55	0·55	0·54
0·002	0·56	0·57	0·56
0·004	0·57	0·57	0·56

This increase in the ratio of D/T is probably to be attributed to the relatively high value of the surface conduction in the capillaries, especially when the concentration of the electrolyte inside them is very low (compare Smoluchowski, *Physikal. Z.*, 1905, **6**, 529; Freundlich, "Kapillarchemie," 2nd edtn., p. 249).

Owing to this surface conduction the resistance of the diaphragm does not diminish proportionately as the electrolyte concentration increases. The total resistance T, on the other hand, is determined mainly by that of the electrolyte, and hence it diminishes almost in proportion to the increase in the electrolyte concentration. The consequence is that the ratio D/T increases with the increasing concentration of the electrolyte. The variation of D/T brings about a corresponding change in the value of the potential across the diaphragm. It is therefore evident that a strict comparison of the results at different concentrations of the electrolytes is only possible when the necessary correction due to this variation has been introduced. In Table I the distance moved by the air bubble corresponds to a potential of 100 volts across the diaphragm. The plus and the minus signs indicate the charge of the diaphragm.

TABLE I.

β-Stannic oxide (water content, 55%).

Concentration of electrolyte (g.-mols.).	p_H values for MgCl$_2$.	BaCl$_2$.	SrCl$_2$.	LiCl.	NaCl.	KCl.
2·00	—	—	—	3·70	4·00	4·16
1·00	3·28	3·34	3·37	3·84	4·09	4·20
0·75	3·36	3·40	3·44			
0·50	3·45	3·47	3·50	3·98	4·16	—
0·25	3·56	3·59	3·61	—	—	—
0·20	—	—	—	4·13	—	—
0·10	3·65	3·68	3·70	—	—	—
0·05	3·68	—	—	—	—	—
0·04	—	—	—	4·22	4·26	4·30
[illegible]	3·78	3·81	3·82	—	—	—

It will be seen from the above data that the capacity of kations to liberate hydrogen ions is in the order $Mg^{\cdot\cdot} > Ba^{\cdot\cdot} >$ Sı $Li^{\cdot} > Na^{\cdot} > K^{\cdot}$. The electro-endosmotic experiments show hydrated stannic oxide is charged negatively in contact with wa and that the capacity of the kations to diminish the negative ch of the surface, as indicated by the movement of the air bubbl in the same order. In the case of the alkali-metal chlorides at concentrations the negative charge of the surface is greater t with pure water. The bivalent kations reverse the negative ch of the surface at as low a concentration as $0{\cdot}0003M$. The centration of the liberated hydrogen ions, however, incre continuously up to a concentration of $1M$ of the bivalent kati This shows that hydrogen ions continue to be liberated even a the surface has become positively charged.

The Adsorption Theory and the Liberation of Hydrogen Ions Kations.—As stannic oxide is negatively charged, it follows f Mukherjee's theory (*loc. cit.*) that the hydrogen ions are held the neighbourhood of the surface by electrostatic attraction. He the greater the capacity of a kation to diminish the negative ch the greater should be its effect on the liberation of hydrogen i and that is what has been observed. The observed reversa electrical charge of stannic oxide by bivalent kations, and change in p_H on repeated washing with barium chloride solu can be explained in exactly the same way as before (Ghosh, *cit.*, p. 2611). The rise in p_H with successive additions of al also admits of a simple explanation. The addition of alkal small amounts simply removes the liberated hydrogen ions, therefore produces the same effect as that of withdrawing original acidic barium chloride solution and replacing it by a f one of p_H 6·6. That the α-oxide contains more replaceable hydr ions, mol. for mol., than the β-oxide, only shows that the for consists of finer particles and hence possesses greater active sur than the latter.

The Adsorption of Anions.

Reference to the electro-endosmotic data shows that at concentrations of the chlorides of the univalent kations the nega charge of hydrated stannic oxide increases. This may be either (1) to the primary adsorption of the anion, or (2) to a re tribution of the kations in the "double layer" leading to an incr in the number of "uncovered" primarily adsorbed anions (w in this case may be the SnO_3H' ion) (compare Mukherjee Iyer, *J. Indian Chem. Soc.*, 1926, **3**, 321). Among the kati potassium has been found to be least effective in diminishing negative charge of the surface. A measurement of adsorptio the same

potassium salts may therefore give some idea of the adsorption of anions, since any adsorption of the salt can in this case be attributed to this cause. For this purpose 10 g. of the substance were shaken in a Pyrex-glass bottle with 100 c.c. of a solution of potassium salt, and after 24 hours the solution was analysed. The results given below (for β-oxide of 54·4% water content) show that there is hardly any primary adsorption of anions :

Weights of salt per 10 c.c.

Initially after correcting for hydration.	After adsorption.	Amount adsorbed.
	KNO_3.	
0·9757 g.	0·9748 g.	+0·0009 g.
0·2442 ,,	0·2450 ,,	−0·0008 ,,
0·0490 ,,	0·0488 ,,	+0·0002 ,,
	K_2SO_4.	
0·1820 g.	0·1809 g.	+0·0011 g.
0·0462 ,,	0·0458 ,,	+0·0004 ,,

Adsorption of Acids and its Relation to Electrical Charge.

A weighed quantity of hydrated stannic oxide was shaken as before (p. 3029) with a measured volume of an acid solution of known strength, and after 24 hours the acid concentration in the supernatant liquid was determined, the *E.M.F.* method being used for low concentrations, and alkali titration for others. As the hydrated oxide contained a large amount of water, a correction had to be introduced for its diluting effect. The amount of adsorption was calculated by multiplying the difference between the corrected initial concentration of the acid and its concentration after adsorption by the total volume of the solution. Tin was not present in the acid solutions within the range of concentrations investigated; the observed adsorption was therefore not due to the formation of any soluble tin salt. The electrical charge was measured by the electro-endosmotic method as previously described. The sample used in Table II is different from that used in the other table. In the following tables a denotes the number of g.-ions of hydrogen adsorbed, and d the distance (in mm.) moved by the air bubble in 2 minutes. In each case 200 c.c. of acid solution were used, together with 20 g. of β-oxide of 54·5% water content.

The electro-endosmotic results show that all the acids, except phosphoric, reverse the initial negative charge of the surface. This indicates that hydrogen ions are primarily adsorbed by the surface. In the case of sulphuric acid, it will be noticed that with increasing concentration the positive charge at first increases, reaches a maximum, and then diminishes again, whereas for nitric

TABLE II.

Initial conc. (corr.).	Final conc.	$a\times10^4$ (obs.).	$a\times10^4$ (calc.).	Initial conc. (corr.).	Final conc.	$a\times10^4$ (obs.).	$a\times10^4$ (calc.).
Sulphuric acid (K_0 = 1·66, K_1 = 188*).				Nitric acid (K_0 = 0·121, K_1 = 28).			
0·124	0·0835	85	83	0·189	0·172	(35·8)	35·8
0·0935	0·0550	(80·8)	80·8	0·143	0·126	34·6	33·6
0·0720	0·0370	73·5	77	0·096	0·082	29·4	30·0
0·0475	0·0170	64	67	0·063	0·052	25·8	25·7
0·0318	0·0082	49·6	53	0·019	0·0134	(11·8)	11·8
0·0186	0·0031	(32·6)	32·6	0·0091	0·006	6·4	6·2
0·0119	0·0015	21·8	19·8	0·0052	0·0036	3·4	3·9
0·0056	0·0007	10·4	10·3	0·00114	0·00075	0·8	0·89
0·0028	0·00037	5·2	5·7				

* K_0 and K_1 are constants (see below), and the values of a which are enclosed in parentheses in each case were used in calculating the corresponding values of the constants.

acid it continues to increase within the range investigated. The ratio of the total change in electrical charge (as indicated by the movement of the air bubble) to the amount of hydrogen ions adsorbed, however, diminishes continuously from the start, showing that with increasing concentration of the acids the electrical adsorption of the anions is preponderating more and more over the primary adsorption of the hydrogen ions. In the above table the calculated values of α were obtained from the expression $K_0C/(1 + K_1C$ (compare Langmuir), where K_0 and K_1 are constants. It can be easily shown that K_0/K_1 is a measure of the active surface.

The agreement between the observed and calculated values is fair. A comparison of the adsorption of the acids with their effect on the electrical charge shows that the adsorption is greater the less the positive charge of the surface. The order of adsorption of the acids is $H_3PO_4 > H_2SO_4 > HCl > HNO_3, CCl_3{\cdot}CO_2H, C_6H_5{\cdot}SO_3H$ The magnitude of adsorption of the monobasic acids is very nearly the same, that of hydrochloric acid, however, being slightly the greatest. The capacity of the different acids to increase the positive charge of the surface is in the order HNO_3, etc.$> HCl > H_2SO_4 > H_3PO_4$. The above results therefore lead to the conclusion that there exists a sort of inverse proportionality between the adsorption of acids and their effect on the positive charge of the surface. This is to be expected also on theoretical grounds: the other factors remaining constant, the chance of a hydrogen ion reaching the surface is the less the greater the positive charge of the surface owing to increasing electrostatic repulsion.

(1) When an acid with a multivalent anion is used, the anion

TABLE III.

[100 C.c. of solution and 10 g. of hydrated β-stannic acid (water content, 54·5%) were used throughout the experiments here recorded.]

Initial conc. (corr.).	Final conc.	$a\times10^4$ (obs.).	$a\times10^4$ (calc.).	Initial conc. (corr.).	Final conc.	$a\times10^4$ (obs.).	$a\times10^4$ (calc.).
Phosphoric acid (K_0 = 0·1, K_1 = 570).				Hydrochloric acid (K_0 = 0·161, K_1 = 55).			
0·177	0·074	108	105	0·0492	0·0316	(18·5)	18·5
0·131	0·038	(97·6)	98	0·0354	0·0206	15·5	15·3
0·097	0·016	85	87	0·0192	0·0102	9·5	10·6
0·0646	0·005	(62·6)	62	0·0118	0·0054	(6·7)	6·7
0·0165	0·0006	16·6	13·4	0·00495	0·0031	4·1	4·3
Trichloroacetic acid (K_0 = 0·073, K_1 = 22·8).				Benzenesulphonic acid (K_0 = 0·064, K_1 = 23·4).			
0·093	0·074	(20·0)	20·0	0·096	0·079	(17·8)	17·8
0·0705	0·054	17·3	17·7	0·076	0·061	15·8	16·2
0·0475	0·034	14·2	13·9	0·0481	0·0366	12·1	12·5
0·024	0·0161	8·2	8·5	0·0244	0·0170	7·8	7·8
0·0121	0·0076	(4·7)	4·7	0·0124	0·0082	(4·4)	4·4
0·0011	0·0038	2·3	2·5	0·0062	0·0043	2·0	2·5
Nitric acid.				Sulphuric acid.			
0·091	0·072	20·0	—	0·071	0·0328	40·0	—
0·0467	0·033	14·3	—	0·0475	0·0146	34·6	—

Electro-endosmotic measurements.

Potential across the diaphragm = 70 volts.
Amount of substance = 16 g.

Initial conc. (corr.).	Final conc.	$a \times 10^4$.	*d.*	Δd.	$\Delta d/a \times 10^3$.
Sulphuric acid. Volume of solution = 200 c.c.					
0·0311	0·0082	49	+ 2·2	6·2	1·3
0·0184	0·0031	32	+ 2·8	6·8	2·1
0·0119	0·0015	20	+ 3·8	7·8	3·9
0·0057	0·0007	10	+ 2·7	6·7	6·7
0·0028	0·00037	5	+ 1·4	5·4	10·8
0	0	0	− 4·0	—	—
Nitric acid. Volume of solution = 200 c.c.					
0·019	0·0134	12	+13·0	17·0	14
0·009	0·006	6·4	+11·0	15·0	23
0·0052	0·00036	3·4	+ 9·7	13·7	40
0·00114	0·00075	0·8	+ 7·2	11·2	140
0	0	0·0	− 4·0	—	—

Potential across the diaphragm = 80 volts.
Amount of substance = 15 g.

Distance (mm.) moved by the air bubble in 2 mins.

Initial

tion of hydrogen ions; moreover, multivalent anions may bring about increase in adsorption of hydrogen ions in another way. (2) When a multivalent anion is electrically adsorbed (or bound) opposite to one of the primarily adsorbed hydrogen ions, all its valencies except one are free, and hence a number of hydrogen ions corresponding to the number of the free valencies of the anion will be drawn near the surface. This will produce the same effect as an increase in the number of primarily adsorbed hydrogen ions. (3) There is yet another factor which may influence the adsorption of hydrogen ions. If the surface be positively charged, there will be an equivalent number of anions surrounding it. Some of these will be free and their number will increase with increasing electrical charge. If these free ions exist in the form of a diffuse layer of thickness, say, δ round the surface, then within this layer the average concentration of hydrogen ions will be much less than in the bulk of the solution. If the electrical charge is reduced to zero or brought to a very low value by increasing the anion concentration, then the value of δ becomes negligibly small and hence a volume of liquid $S\delta$ (where S is the total solid–liquid interfacial area) which was formerly only partly accessible to the hydrogen ions now becomes completely so. This will also produce an apparent increase in the adsorption of hydrogen ions.

Effect of Neutral Salts on the Adsorption of Hydrogen Ions.

The effect of electrical charge on the adsorption of acids can also be tested in the following way. If the concentration of the hydrogen ions be maintained constant and that of the anion is increased by adding a neutral salt with an inactive kation, the positive charge of the surface will be diminished, and hence the adsorption of hydrogen ions will be greater in presence of a neutral salt than in its absence. It will be seen from the previous experiments that of all the kations the potassium ion is the least active; potassium salts were therefore used in the following experiments. The adsorption of acid was measured as previously described.

It will be observed that the adsorption of nitric acid is considerably greater in presence of potassium nitrate than in its absence. When the concentration of the salt is kept constant and that of the acid varied, the percentage rise in adsorption increases with the decreasing concentration of the acid. Again, keeping the concentration of nitric acid constant and increasing that of the salt, the adsorption of the acid is found to increase. Here we are not dealing with any multivalent anion, and hence increase in adsorption is to be attributed to the diminution of the positive charge of the surface and also of the thickness of the diffuse layer δ.

TABLE IV.

Amount of substance taken, 10 g. (water content, 54·5%); volume of solution = 100 c.c.

Initial concs. (corr.).		Final conc. of acid.	Amount of acid absorbed (as c.c. of 0·2N).
Mixtures of HNO_3 + KNO_3.			
HNO_3.	KNO_3.		
0·091	0	0·072	10·0
0·093	0·25	0·069	12·5
0·0467	0	0·0334	7·0
0·0475	0·25	0·0296	9·4
0·024	0	0·0154	4·5
0·024	0·25	0·0092	7·8
0·0244	0·1	0·0110	7·1
0·0244	0·05	0·0124	6·3
Mixtures of HNO_3 + K_2SO_4.			
HNO_3.	K_2SO_4.		
0·0910	0	0·0720	10·0
0·0940	0·2	0·0490	23·7
0·0467	0	0·0334	7·0
0·0467	0·2	0·0129	17·7
Mixtures of H_2SO_4 + K_2SO_4.			
H_2SO_4.	K_2SO_4.		
0·0495	0	0·0154	18·0
0·0481	0·2	0·0158	17·0
0·0491	0·05	0·0156	17·6

The adsorption of hydrogen ions is much greater in the nitric acid–potassium sulphate mixture than in nitric acid and potassium nitrate. In this case, in addition to the two factors mentioned above, the effect of the multivalent anions makes itself felt. In the sulphuric acid–potassium sulphate mixture the adsorption of acid is not at all increased : on the contrary, a slight decrease in adsorption is observed. This is not surprising, for in presence of 0·015N-sulphuric acid the charge of the surface is very small (nearly zero), and hence an increase in the number of SO_4'' ions is not likely to favour any further adsorption. The $K^{\cdot}$ ions on the other hand can displace from the mobile layer some of the hydrogen ions associated with the electrically adsorbed SO_4'' ions, and thus slightly decrease the adsorption.

The Variation of Active Surface with the Amount of Substance taken.—It has been emphasised that in the interaction of stannic oxide with electrolytes it is the solid–liquid interface that is directly taking part in the reaction. The question arises as to how the active surface increases with the amount of substance taken. It has already been mentioned that K_0/K_1 is a measure of the active surface. Therefore, by taking different quantities of stannic oxide and determining the values of K_0 and K_1 for each quantity, it is possible to find how the active surface varies with the amount of substance. The adsorption of acid was measured as before. 100 C.c.

of a sulphuric acid solution were used, with 10 g. of the β-oxid (water content, 54·5%) in the first case and 5 g. in the second.

	Initial conc. (corr.).	Final conc.	$a \times 10^8$.	K_0.	K_1.	K_0/K_1.
(1)	0·071	0·0328	4·0	1·03	228	0·0045
	0·0475	0·0146	3·46			
(2)	0·073	0·052	2·14	0·44	186	0·0024
	0·049	0·0295	1·99			

It will thus be seen that the active surface increases in the rati 1 : 1·9 as the amount of substance is doubled.

Summary.

1. A study of the interaction of hydrated stannic oxides wit electrolytes shows that the adsorption theory offers a much bette explanation of the observed facts than the chemical theory o insoluble salt formation.

2. In accordance with Mecklenburg's views, the α-oxide has been found to possess greater active surface per unit weight, and hence finer particles, than the β-oxide.

3. The capacity of the kations to liberate hydrogen ions is in the order $Mg^{\cdot\cdot} > Ba^{\cdot\cdot} > Sr^{\cdot\cdot} > Li^{\cdot} > Na^{\cdot} > K^{\cdot}$, and, in satisfactory agreement with Mukherjee's theory, the same order has been observed in their effect on the negative charge of the surface.

4. The electro-endosmotic results indicate that the hydrogen ions are primarily adsorbed, and the adsorption of an acid is greater the less the positive charge of the surface. The order of adsorption of the acids is $H_3PO_4 > H_2SO_4 > HCl > HNO_3, C_6H_5{\cdot}SO_3H, CCl_3{\cdot}CO_2H$. The capacity of the acids to increase the positive charge of the surface is in the order HNO_3, etc.$> HCl > H_2SO_4 > H_3PO_4$. This leads to the conclusion that the greater the capacity of the anion to diminish the positive charge of the surface the greater is the adsorption of the hydrogen ions. The adsorptions of the kations and anions are thus not independent of each other.

5. In presence of salts with inactive kations, the adsorption of hydrogen ions is increased. In this respect, salts with multivalent anions are more effective than those with univalent anions.

6. The active surface has been found to vary nearly proportionately with the amount of substance.

In conclusion, I take this opportunity of expressing my most sincere thanks to Professor F. G. Donnan, C.B.E., F.R.S., for his advice and encouragement.

CCCXCVIII.—*The Effect of the Spatial Position of Substituent Groups on Acidic Strength.*

By Bernhard Flürscheim.

Some years ago (J., 1909, **95**, 718; 1910, **97**, 84), I attempted to show that the electrolytic equilibria of acids, bases, and salts depend on the same three internal (constitutional) factors p, q, and s which determine reactions in general. In so far as the steric factor (s) is concerned, I suggested that the rate of association of ions is retarded by spatial obstruction, whereas the reverse process of dissociation into ions remains unaffected, so that *ceteris paribus* steric hindrance must raise the dissociation constant. In support of this view, the relative steric effects on dissociation constants were shown to run parallel to the relative steric inhibitions of other reactions; the order for different substituents and positions being:

$$I > Br, C_6H_5 > Cl, O, N, C(CH_3, CO) > H;$$

o- > β- > α-; and γ-, δ-, *m*-, *p*-, side-chain in *o*- almost = 0. The evidence included a correlation of the dissociation constants of more than 100 acids and bases and of the dissociation constants and relative hydrolysis of certain organic salts by means of semi-quantitative evaluations of the steric and the other two effects. Later (*Trans. Faraday Soc.*, 1923, **19**, 531; *Phil. Mag.*, 1924, **47**, 569) I suggested that the remarkable extent to which the approach even of a hydrogen ion can be inhibited sterically by substituents in the anion is intelligible in view of Lapworth's proof that hydrogen ions are solvated.

Independent evidence for the steric effect in electrolytic equilibria was found by me (*Chem. and Ind.*, 1925, **44**, 249) in the dissociation constants of certain ethylenic isomerides. Since the ratio of these constants for α-bromo*allo*cinnamic acid/α-bromocinnamic acid = maleic acid/fumaric acid = 15 (approx.), and *iso*crotonic acid/crotonic acid > 1, and since p and q must be identical for the *cis*- and the *trans*-form of the same acid, the conclusion was drawn that the greater strength of each *cis*-form must be due to a pure steric effect in the above sense; if it were a *polar* effect across space, the ratio K_{cis}/K_{trans} would be smaller for the α-bromocinnamic acids (effect of phenyl) than for maleic and fumaric acids (effect of carboxyl), and would be less than 1 for the crotonic acids (effect of methyl).

A recent paper by D. H. Hey (this vol., p. 2321) deals wholly with this question of the steric effects on acidic strength. This author has evidently overlooked the papers mentioned above, for [illegible]

Contrary to the general assumption that ionic reactions are instantaneous, the introduction of a steric delay in association implied, of course, that association of ions is a time reaction, from which it follows that dissociation must also be a time reaction (governed, I suggest, by the internal factors p and q); if dissociation alone were instantaneous, it would always be practically complete. The principle of ionic time reactions has recently also been advocated by Brönsted and Pedersen (*Z. physikal. Chem.*, 1924, **108**, 230) and Brönsted (*Ber.*, 1928, **61**, 2050, footnote), who suggest that it is therefore "possible, but not very probable, that the same equilibrium (strength) might be determined by very different values of the absolute velocities of dissociation and association." The introduction of a steric factor, however, for association alone transforms such a remote contingency into a virtual certainty. Thus *o*-chloro- and *o*-iodo-benzoic acid have approximately the same dissociation constant; let k_1 and k_2, respectively, be the rates of dissociation and association in the chloro-acid, and $m \times k_1$ and $n \times k_2$ those in the iodo-acid, then we have (compare J., 1909, **95**, 731) $m < 1$ (since p for I < Cl) and $n < 1$ (since s for I > Cl); whenever $m = n$, the dissociation constants of the two acids are, of course, identical ($= k_1/k_2$), and this is what approximately applies in the present case.

Spiers and Thorpe (J., 1925, **127**, 538) introduced an "approach effect" brought about by altered valency direction. Where primary dissociation constants are concerned, this approach effect is obviously a special case of the steric effect postulated by me, for which these authors' observations supply further valuable evidence. In cases of secondary dissociation, however, the electrostatic effect of the first charge on the charges involved in the secondary dissociation (Ostwald, *Z. physikal. Chem.*, 1892, **9**, 558; Bjerrum, *ibid.*, 1925, **106**, 219) may, and usually will, outweigh all other factors (*e.g.*, in the classical example, secondary dissociation constant of maleic acid < fumaric acid). In view of what has been said above, Spiers and Thorpe's remark on my views—"no explanation is offered as to how this steric influence is produced"—can hardly be upheld.*

* Quite recently (*Ber.*, 1928, **61**, 1524), the possibility of a steric inhibition of the association of ions has also been admitted by Hückel; and since the above was written, the steric effect on the tautomerism of kations

CCCXCIX.—*Pentanitroaniline.*

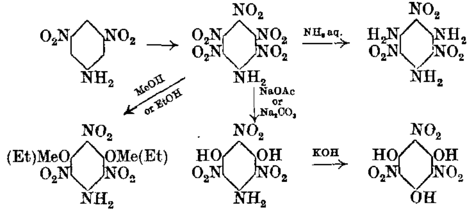
By BERNHARD FLÜRSCHEIM and ERIC LEIGHTON HOLMES.

PRELIMINARY experiments had indicated (Flürscheim and Simon, P., 1910, **26**, 81) that when 3 : 5-dinitroaniline is nitrated in mixed acid, " a nitroamine is first formed, which is subsequently converted into a compound which may be pentanitroaniline." At that time, this " compound " had only been obtained in a very impure condition and in very poor yield, so that its nature could not be definitely ascertained. The investigation of this reaction has now again been taken up.

3 : 5-Dinitroaniline and *m*-nitroaniline behave quite differently towards mixed acid. In both cases, nitroamides are primarily formed, but whereas with *m*-nitroaniline these remain in solution (provided that the acid is sufficiently concentrated), so that the first and only product which separates is pure 2 : 3 : 4 : 6-tetranitroaniline, 3 : 5-dinitroaniline gives rise to sparingly soluble nitroamides. Their rearrangement to the corresponding nuclear nitro-derivatives is retarded by their low solubility, and before it can be completed, they decompose—unless special precautions are taken—with violent flashes. When, however, such decomposition is prevented, the colour gradually changes from orange-red to deep yellow, corresponding to a transition of the nitroamides into nearly pure pentanitroaniline. The latter can be obtained quite pure by recrystallisation from benzene; one molecule of benzene is retained at first, but can be easily removed.

In most respects, the chemical and physical properties of pentanitroaniline are similar to those of tetranitroaniline. For instance, both compounds are golden-yellow; both melt with decomposition near 200° (the latter at 216—217°, the former at 192°; heating at the rate of 5° per minute). Both, when dropped into a red-hot crucible, a few centigrams at a time, flash without detonation and with the formation of mere traces of carbon. In both, the nitro-groups in the meta-positions (one in tetranitroaniline, two in pentanitroaniline) are readily replaced, and the amino-group less readily, by the same reagents, corresponding derivatives being formed in either case. In this way, just as numerous penta-sub-

reactions have been carried out represented by the following formulæ :



These transformations prove that all five nitro-groups are in the nucleus—as was to be expected, since pentanitroaniline has not the properties of a nitroamide.

In two directions only has pentanitroaniline been found to differ essentially from tetranitroaniline : its greater solubility in organic solvents, and its behaviour on acetylation. The table of approximate solubilities given below for 2 : 4 : 6-trinitroaniline, tetranitroaniline and pentanitroaniline reveals marked differences and, it seems, no connexion between the number of nitro-groups and the solubility in a given solvent. On acetylation by means of acetic anhydride with a little concentrated sulphuric acid, tetranitroaniline yields its acetyl derivative, but from pentanitroaniline an acetyl derivative is produced in which at least one nitro-group has been replaced. Preliminary tests appear to indicate that this compound does not belong to the series obtained by the removal of *m*-nitro-groups, so that the possibility that acidic reagents may replace a *p*-nitro-group must be examined; it should be remembered that in pentanitroaniline even the *p*-nitro-group has two other nitro-groups adjacent to it.

The work is being continued.

EXPERIMENTAL.

Pentanitroaniline.—1 Part of 3 : 5-dinitroaniline, prepared by Flürscheim's modification of Bader's method (*J. pr. Chem.*, 1905 **71**, 537), is dissolved in 20 parts (by volume) of oleum (5%) and 1·5 parts (by volume) of nitric acid (*d* 1·52) are added below The solution is then heated at 70—75° for 3 hours *without sh*

The spent acid is removed by suction, and the product (nearly pure pentanitroaniline, decomp. 189°) recrystallised from benzene. Up to 3 g. of 3 : 5-dinitroaniline have, so far, been nitrated at a time,* giving an average yield of 1·5 g. of pure pentanitroaniline (containing 1 mol. of benzene) per 3 g. of 3 : 5-dinitroaniline used. Pentanitroaniline crystallises with 1 mol. of benzene in golden-yellow prisms. Dr. I. Knaggs, of the Davy Faraday Laboratory, who very kindly examined these microscopically, informs us that they are either monoclinic or triclinic, a decision between these alternatives not being feasible without detailed measurements. The ground material, when brought to constant weight by 18 hours' exposure in a vacuum at room temperature, lost 19·6% in weight ($C_6H_2O_{10}N_6,C_6H_6$ requires C_6H_6, 19·7%). The crystals remain unaffected in shape and colour by the loss of benzene, but become opaque. Benzene-free *pentanitroaniline* melts at 192° with rapid decomposition, after darkening to a deep orange at 160—170° (rate of heating 5° per minute) (Found : C, 22·7; H, 0·65; N, 26·45, 26·4. $C_6H_2O_{10}N_6$ requires C, 22·6; H, 0·6; N, 26·4%). Approximate comparative solubilities are given in the following table :

	2 : 4 : 6-Trinitro-aniline.	Tetranitro-aniline.	Pentanitro-aniline.
Benzene.	0·025 g. in 0·5—1·0 c.c. at 74·5°. Cryst.	0·02 g. in 5—6 c.c. at 74·5°. Cryst.	0·023 g. in less than 0·5 c.c. at 74·5°. Cryst.
Acetic acid.	0·019 g. in 0·25—0·5 c.c. at 75°. Cryst.	0·025 g. in 0·95—1·2 c.c. at 75°. Cryst.	0·019 g. in less than 0·2 c.c. at 20°. No cryst.
Acetone.	0·030 g. in 0·25—0·4 c.c. at 50°. Cryst.	0·021 g. in 0·25—0·4 c.c. at 50°. No cryst.	0·024 g. in less than 0·1 c.c. at 20°. No cryst.
H_2SO_4 (100%).	0·021 g. in less than 0·3 c.c. at 20°. No cryst.	0·020 g. in 4·5—5·0 c.c. at 75°. Cryst.	0·023 g. in 11·5—13·5 c.c. at 75°. No cryst.

"Cryst." or "no cryst." indicates whether or no the nitro-compound crystallises on cooling in running water. The lower values, for c.c. used, indicate a deficiency, the higher values an excess, of solvent required for complete solution.

From 3 : 5-dinitroacetanilide a lower yield of pentanitroaniline was obtained than from dinitroaniline itself : 4·5 g. of the acetyl derivative, nitrated in 80 c.c. of sulphuric acid monohydrate with 6·0 c.c. of nitric acid (*d* 1·52) for 6 hours at 65—70°, gave only 0·6 g.

* An improved method of nitrating 3 : 5-dinitroaniline which we have since found (in which 1 part of this amine in 40 parts by vol. of 100% sulphuric acid and 2·5 parts by vol. of nitric acid, *d* 1·52, is heated to 75° during ½ hour and kept at 75° for 1 hour) avoids the separation of nitroamides altogether, and thereby makes it possible to nitrate any desired amount at a time and

of pentanitroaniline; and 12·3 g., nitrated with the same proportions of oleum (5% SO_3) and nitric acid as were used for the amine, gave in 5 hours at 65—70° only 1·5 g. of pentanitroaniline.

2 : 4 : 6-*Trinitro-5-aminoresorcinol*.—To a solution of 0·50 g. of benzene-free pentanitroaniline in 5 c.c. of acetone, an excess of aqueous sodium acetate was added gradually with good shaking. The solution, which turned red with some effervescence, was frequently shaken during ½ hour, the acetone driven off, and an excess of concentrated hydrochloric acid added to the residue. The yellow precipitate obtained (m. p. 220°, decomp.) crystallised from benzene–alcohol in small deep yellow crystals, m. p. 236—237° (decomp.) (heating, 5° per minute). This *compound* was obtained in brownish-yellow, fine needles of the same m. p. and mixed m. p. when 1 g. of pentanitroaniline was heated on a water-bath with 10 c.c. of saturated sodium carbonate solution, with subsequent dilution with water, until the separated sodium salt had redissolved, and precipitation with hydrochloric acid. Yield, 0·609 g. of crude material (decomp. 230°), which was recrystallised from water (Found : N, 21·8. $C_6H_4O_8N_4$ requires N, 21·5%).

2 : 4 : 6-*Trinitrophloroglucinol*.—1 G. of benzene-free pentanitroaniline in 10 c.c. of a saturated sodium carbonate solution and 10 c.c. of water was heated until it dissolved, 10 c.c. of 10% aqueous potassium hydroxide were then added, and heating was continued on a water-bath until the evolution of ammonia had ceased. Water was added, to redissolve the separated potassium salt, followed by an excess of hydrochloric acid. After evaporation in a vacuum over sulphuric acid, the compound was extracted with ether (yield, 0·562 g.). Trinitrophloroglucinol is very soluble in hot water and appreciably soluble in cold water, but it can easily be recrystallised from water by adding a very little hydrochloric acid, whereby the solubility is much reduced. It was thus obtained in characteristic, long, spear-like crystals with an ochre colour, m. p. 167° (in agreement with Jackson and Warren, *Amer. Chem. J.*, 1893, **15**, 615) after prior heating to remove water of crystallisation (Found : N, 16·1. Calc. : N, 16·1%).

2 : 4 : 6-*Trinitro-5-aminoresorcinol Dimethyl Ether*.—Benzene-free pentanitroaniline (2·8 g.) was refluxed for 6 hours with 28 c.c. of dry methyl alcohol and then cooled. A little bicarbonate solution was added to transform traces of free hydroxy-compounds into their salts, and the *ether* was then precipitated by an excess of water (yield, 1·76 g.; m. p. 125°). After recrystallisation from ethyl acetate–ligroin it had m. p. 127—127·5°, and after further recrystal-

C, 33·3; H, 2·8: N, 19·4%). A small quantity of a mixture of bicarbonate-soluble hydroxy-compounds was isolated. These must be produced by the action of traces of water during the replacement of the nitro-groups, since the ether, once formed, is not attacked even by boiling aqueous methyl alcohol; from 0·5 g. of the ether, after 2 hours' boiling with 95% methyl alcohol, 0·496 g. was recovered unchanged.

2 : 4 : 6-*Trinitro-5-aminoresorcinol Diethyl Ether*.—This was prepared in a similar manner from 2 g. of benzene-free pentanitroaniline and 20 c.c. of dry ethyl alcohol (yield, 1·176 g.; m. p. 123°). After solution in alcohol, and retreatment with bicarbonate and water as above, the *ether* had m. p. 125—126°, which became constant at 127·25—127·75° after successive recrystallisations from alcohol and petrol. The product crystallised in yellow blades (Found: C, 38·0; H, 3·9; N, 17·95, 18·1. $C_{10}H_{12}O_8N_4$ requires C, 38·0; H, 3·8: N, 17·7%). The dimethyl and diethyl ethers have the same melting point; a mixture of the two, however, melts at a lower temperature.

2 : 4 : 6-*Trinitro*-1 : 3 : 5-*triaminobenzene*.*—1·000 G. of benzene-free pentanitroaniline was gradually added to 18 c.c. of 10% aqueous ammonia. The material instantly became red, then light brown on shaking. After boiling, an orange-yellow powder (0·670 g.) was obtained corresponding to the description of trinitro-1 : 3 : 5-triaminobenzene given by Jackson and Wing (*Amer. Chem. J.*, 1888, **10**, 282), being insoluble in nearly all solvents, but recrystallisable from aniline, and showing no signs of melting up to 300° (Found: N, 32·6. $C_6H_6O_6N_6$ requires N, 32·6%). The symmetrical constitution of this compound, involving the adjacency of two nitro-groups to each amino-group, is confirmed by the fact that 0·030 g., dissolved in 1·84 g. of concentrated sulphuric acid, is precipitated by 0·15 g. of water.

Acetylation of Pentanitroaniline.—Pentanitroaniline (0·42 g.) did not react with 5 c.c. of acetic anhydride and two drops of concentrated sulphuric acid on heating on a water-bath for 15 minutes, the cooled solution being subsequently poured on ice. When, however, 0·5 g. of benzene-free pentanitroaniline was *boiled* with 5 c.c. of acetic anhydride and two drops of concentrated sulphuric acid, either for 5 minutes, or better for only a few seconds, followed by immediate water-cooling, the excess of acetic anhydride then being

* Addendum.—We have since succeeded in reducing this compound to hexa-aminobenzene, a crystalline compound, readily soluble in water, which melts and decomposes at about 255° (rate of heating, 30° per min.), slowly darkens in the air, gives a hexa-acetyl derivative (not melted at 300°) and a

mostly removed in a vacuum and the residue mixed with sno a solid was obtained which crystallised from benzene or fro petrol (b. p. 100—120°) in almost colourless, short, sword-shap crystals of constant m. p. 147—147·5°. Yield (in the case of on brief boiling), 0·25 g. (Found: N, 18·9. A tetranitrodiacetamid phenol, $C_{10}H_7O_{11}N_5$, requires N, 18·8%). The nitrogen content this compound makes it certain that at least one nitro-group h been replaced, but preliminary tests with the small amount availab on its behaviour toward sodium acetate and ammonia render probable that the replaced nitro-group did *not* occupy one of tl meta-positions.

Acetylation of Tetranitroaniline.—When tetranitroaniline w treated similarly, *viz.*, 0·8 g. boiled for 5 minutes with 8 c.c. acetic anhydride and three drops of concentrated sulphuric aci most of the acetic anhydride removed in a vacuum, and snow adde 0·76 g. of crude tetranitroacetanilide, m. p. 163—164° (decomp (heating at the rate of 5° per minute), was obtained. This con pound, which has been mentioned (P., *loc. cit.*) but not describe forms, on recrystallisation from benzene–glacial acetic acid, slightl yellow, small needles, decomp. 169° (constant) (Found: N, 22· $C_8H_5O_9N_5$ requires N, 22·2%). Acetylation in this case, therefor is not attended by the removal of a nitro-group.

We desire to record our obligation to the Advisory Council of tl Department of Scientific and Industrial Research for a grant to o of us (E. L. H.); also to Sir W. H. Bragg and the Royal Institutio who have enabled us to utilise the excellent facilities of the Dav Faraday Laboratory, where this work was carried out.

[*Received, October 8th*, 1928.]

CCCC.—*The Synthesis of Four Amino-3-hydroxy-1 : 4-benzisooxazines.*

By George Newbery and Montague Alexandra Phillips.

Of the four possible amino-3-hydroxy-1 : 4-benz*iso*oxazines in whic the amino-group is in the benzene ring, only the 6-amino-derivati has hitherto been described (Howard, *Ber.*, 1897, **30**, 2103). A the characterisation of these isomerides was necessary for th orientation of certain of their arsinic acid derivatives, their synthes

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means of alkali and subsequent reduction, melted at 255°, whereas Howard (*loc. cit.*) gives 225°. The same product, m. p. 255°, was also obtained by the reduction of 2 : 4-dinitrophenoxyacetic acid.

The nitration of 4-acetamidophenoxyacetic acid, followed by hydrolysis, and the nitration of 4-aminophenoxyacetic acid by Howard's method gave the same nitro-4-aminophenoxyacetic acid. On reduction, 6-amino-3-hydroxy-1 : 4-benz*iso*oxazine, m. p. 255°, was obtained.

The basicity of 5-*amino*-3-*hydroxy*-1 : 4-*benz*iso*oxazine* is of a lower order than that of its isomerides; *e.g.*, 1½ mols. of $N/10$-mineral acid are required for its solution, whereas the others dissolve in 1 mol. of $N/10$-acid to give salts which are neutral to Congo-red. The other isomerides diazotise normally, but the 5-isomeride forms with nitrous acid a *triazole* which crystallises with a molecule of water; this cannot be driven off at 120° and the triazole may therefore have the constitution

$$\begin{array}{l} \quad\quad\;\; O\cdot CH_2 \\ C_6H_3 \begin{array}{l} < \\ > \end{array} \quad | \\ N{=}N \; > N\cdot C(OH)_2. \end{array}$$

EXPERIMENTAL.

(A) 5-*Amino*-3-*hydroxy*-1 : 4-*benz*iso*oxazine*.—3-Nitro-2-aminophenol, obtained by Fourneau (*Bull. Soc. chim.*, 1927, **41**, 499) by the de-arsenication of 3-nitrobenzoxazolone-5-arsinic acid and by King (J., 1927, 1059) in small yield by nitration in acetic anhydride of *ON*-diacetyl-*o*-aminophenol (Ingold and Ingold, J., 1926, 1321), was obtained in improved yield by treating the crude nitration product as follows:

45 G. were boiled under reflux with hydrochloric acid (150 c.c.; *d* 1·16) for 45 minutes; 190 c.c. of 10*N*-sodium hydroxide were added to the cooled solution, which, still acid to Congo-red, was then boiled with charcoal and filtered. On cooling, 3-nitro-2-aminophenol (17 g., m. p. 217°) separated. The addition of a further 25 c.c. of 10*N*-sodium hydroxide gave a mixture (4·7 g., m. p. 180—185°). By rendering the liquor, which was still acid to Congo-red, neutral to litmus, 5-nitro-2-aminophenol (5·6 g., m. p. 200°) was obtained (total yield of nitro-2-aminophenols, 94%). The mixture of m. p. 180—185°, on similar fractional neutralisation of its solution in acid, gave 1·5 g. each of the above nitroaminophenols. The total yields isolated are thus 63·5 and 24·4% of the 3- and 5-nitro-2-aminophenols, respectively, which are considerably at variance with those estimated by Ingold and Ingold (*loc. cit.*).

The mother-liquors on extraction with ether gave a mixture of

sodium acetate to its solution in warm concentrated hydrochloric acid, in red needles changing to hexagonal plates, m. p. 212°. The mono- and di-acetyl derivatives agreed in m. p. with those described by Ingold and Ingold (*loc. cit.*).

3-*Nitro-2-chloroacetamidophenol.* To 3-nitro-2-aminophenol (10 g.) in acetone (80 c.c.), chloroacetyl chloride (8 c.c.) was added with shaking (temp. 25°). After 30 minutes, the bulk of the acetone was removed. The *chloroacetyl* derivative, which slowly separated (11·5 g.; 88%), crystallised from alcohol in yellow prisms, m. p. 153—154°, readily soluble in organic solvents but insoluble in water (Found: N, 12·0; Cl, 15·2. $C_8H_7O_4N_2Cl$ requires N, 12·1; Cl, 15·4%).

5-*Nitro-3-hydroxy-*1 : 4-*benzisooxazine.* A paste of 3-nitro-2-chloroacetamidophenol (6 g.) and water (5 c.c.) was treated with 2*N*-sodium hydroxide (20 c.c.) and heated in a boiling water-bath for 30 minutes. On acidification, the *product* separated in orange prisms (4·9 g.; 98%), m. p. 115—116°. The solution in boiling water (50 parts) deposited, on cooling, long, prismatic needles of the same m. p. (Found: N, 14·2. $C_8H_6O_4N_2$ requires N, 14·4%).

5-*Amino-3-hydroxy-*1 : 4-*benzisooxazine.* A mixture of the above nitro-compound (3 g.) with iron powder (6 g.) was added to boiling water (60 c.c.) containing glacial acetic acid (3 c.c.). After short boiling, the mixture was made faintly alkaline to litmus with 2*N*-sodium hydroxide and boiled with an equal volume of water. The *product* crystallised, on concentration of the filtered solution, in colourless prisms (1·6 g.; 73%), m. p. 236° after recrystallisation. It is moderately easily soluble in alcohol (Found: N, 16·9. $C_8H_8O_2N_2$ requires N, 17·1%). The *hydrochloride* formed characteristic rhombs, hydrolysed by boiling water (Found: N, 14·0; Cl, 17·3. $C_8H_8O_2N_2,HCl$ requires N, 13·9; Cl, 17·7%). The *acetyl derivative* (Found: N, 13·3. $C_{10}H_{10}O_3N_2$ requires N, 13·6%) crystallised from alcohol in colourless prisms, m. p. 255°. The *triazole*, made by addition of sodium nitrite (1 mol.) to a suspension of the hydrochloride in cold water, crystallised from boiling water in plates, m. p. 204° (Found: N, 21·7. $C_8H_5O_2N_3,H_2O$ requires N, 21·8%).

(B) 6-*Amino-3-hydroxy-*1 : 4-*benzisooxazine.*—(a) When a mixture of 2 : 4-dinitrophenoxyacetic acid (Pratezi, *Gazzetta*, 1892, **21**, 402; m. p. 147—148°; 24 g.), iron filings (63 g.), water (100 c.c.), and hydrochloric acid (25 c.c.; *d* 1·16) was warmed, a vigorous reaction set in which was controlled when necessary by cooling. After a further 15 minutes' heating, the liquid was filtered and treated with a large excess of hydrochloric acid. The hydrochloride,

ric oxide with boiling water, weighed 9·5 g. (47·5% yield) and ystallised in plates, m. p. 300° (decomp.) (Found : N, 13·7; Cl, ·6%). The base (colourless prisms, m. p. 255° after crystallis-ion from alcohol) was obtained by treatment of the hydrochloride lution with sodium acetate (Found: N, 17·1%). The *acetyl* rivative (fine needles from water) melted at 298—299° (bath at 0°) (Found : N, 13·5%).

(b) 4-*Nitro-2-chloroacetamidophenol*, prepared from 4-nitro-2-ninophenol, crystallised from alcohol in stout hexagonal plates, . p. 245° (decomp.). It was insoluble in water and ether and aringly soluble in alcohol and acetone (Found : N, 12·0; Cl, ·5%).

6-*Nitro-3-hydroxy-*1 : 4-*benzisooxazine* formed almost colourless isms from alcohol; m. p. 233—234°, depressed by admixture th the 7-nitro-compound, m. p. 232°. It was insoluble in water d sparingly soluble in alcohol and acetone (Found : N, 14·6%). n reduction with iron and boiling dilute acetic acid it gave the rresponding amino-derivative, m. p. 255°.

(c) 4-Acetamidophenoxyacetic acid (5·8 g.) mixed with potassium trate (2·9 g.) was added to sulphuric acid (30 c.c.) at 10°. After hour the mixture was poured on ice; 2-*nitro-4-acetamidophenoxy-etic acid* (5·8 g.; 82%) then crystallised, and was obtained in llow rhombic plates, m. p. 205—206°, by recrystallisation from ater. It was readily soluble in alcohol and sparingly soluble in her organic solvents (Found : N, 10·7. $C_{10}H_{10}O_6N_2$ requires N, ·0%). On hydrolysis with 7*N*-hydrochloric acid it gave 2-nitro-aminophenoxyacetic acid (m. p. 196°; yield, 92%), identical with at obtained by the nitration of 4-aminophenoxyacetic acid loward, *loc. cit.*). Both the nitroamino-acid and its acetyl deriv-ive, on reduction by tin and hydrochloric acid, gave 6-amino-hydroxy-1 : 4-benz*iso*oxazine, m. p. 255°, not depressed by lmixture with the products from (a) and (b).

(C) 7-*Amino-3-hydroxy-*1 : 4-*benzisooxazine*.—5-*Nitro-2-chloroacet-nidophenol*, prepared from 5-nitro-2-aminophenol, crystallised om alcohol in light yellow prisms or tetrahedra, m. p. 233° (de-mp.). It was insoluble in cold water (Found : N, 12·1; Cl, ·5%).

7-*Nitro-3-hydroxy-*1 : 4-*benzisooxazine* formed yellow prisms, m. p. 32°, from alcohol (Found : N, 14·0%).

7-*Amino-3-hydroxy-*1 : 4-*benzisooxazine* separated in colourless isms, m. p. 220°, from boiling water. It is insoluble in cold water d ether, slightly soluble in chloroform and moderately easily

prisms, readily soluble in cold water to give a solution neut Congo-red (Found : N, 14·0; Cl, 17·5%).

7-*Acetamido-3-hydroxy*-1 : 4-*benzisooxazine* was deposited fro water in fine needles, m. p. 250°. It is insoluble in cold ether, and chloroform and moderately easily soluble in a (Found : N, 13·3%).

(D) 8-*Amino-3-hydroxy*-1 : 4-*benzisooxazine*.—The methods in the literature for the formation of 6-nitro-2-aminophenol the de-arsenication of 2-nitro-4-acetamido-3-hydroxyphenyla acid (Benda, *Ber.*, 1914, **47**, 1010) and the nitration of *o*-aceta phenol in acetic anhydride (King, *loc. cit.*), are not satisfacto the preparation of large quantities. The following method therefore used :

3 : 5-Dinitro-4-hydroxyphenylarsinic acid (120 g.) was ref for 1 hour with sodium bisulphite (60 g.) in water (400 c.c further 60 g. of sodium bisulphite in water (100 c.c.) were added, and the boiling continued for 3 hours. After coolin supersaturated solution of sodium sulphate decahydrate decanted from the cake of 2 : 6-dinitrophenol, which was cryst from 50% alcohol (m. p. 60°; yield, 54 g. or 75%). On red by ammonium sulphide (Post and Stuckenberg, *Annalen*, **205**, 85), and crystallisation from alcohol, a 45% yield of 6- 2-aminophenol, m. p. 112—113° (Found : N, 17·9. Calc. 18·2%), was obtained. The *acetyl* derivative was obtained monohydrate, m. p. 102—103°; the anhydrous substance mel 122° (Found : N, 15·0. $C_8H_8O_4N_2$ requires N, 14·9%).

6-*Nitro-2-chloroacetamidophenol* crystallised from alcohol in yellow rhombs, m. p. 126°, insoluble in water and sparingly so in cold acetone (Found : N, 11·8; Cl, 15·6%).

8-*Nitro-3-hydroxy*-1 : 4-*benzisooxazine* formed light yellow p m. p. 255°, from alcohol (Found : N, 14·3%).

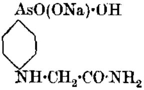
8-*Amino-3-hydroxy*-1 : 4-*benzisooxazine* (Found : N, 17·0%) f colourless prisms, m. p. 180°, from water. It formed a h chloride, m. p. 272° (decomp.), and an acetyl derivative, 257°. This compound and its derivatives were identical with obtained previously by Dr. I. E. Balaban in this laborato 3070).

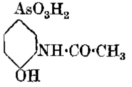
RESEARCH LABORATORY, MESSRS. MAY & BAKER, LTD.,

CCCCI.—*Heterocyclic Compounds containing Arsenic. Part II. Derivatives of* 1 : 4-*Benzisooxazine.*

By George Newbery, Montague Alexandra Phillips, and Ralph William Ewart Stickings.

The therapeutic importance of tryparsamide (sodium hydrogen phenylarsinate 4-glycineamide; I) and of stovarsol (3-acetamido-4-hydroxyphenylarsinic acid; II) suggested the desirability of preparing some hitherto undescribed products of the type of 3-*hydroxy*-1 : 4-*benzisooxazine*-6-*arsinic acid* (III) for pharmacological comparison.


(I.)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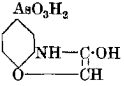
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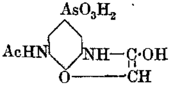
The arsinic acid (III) was first prepared by reduction of 2-nitrophenoxyacetic acid 4-arsinic acid, the intermediate 2-amino-compound losing water under the conditions employed. It was also obtained from 3-chloroacetamido-4-hydroxyphenylarsinic acid (Raiziss and Fisher, *J. Amer. Chem. Soc.*, 1926, **48**, 1326), which readily loses hydrogen chloride in alkaline solution. Similarly, 3-chloroacetamido-5-acetamido-4-hydroxyphenylarsinic acid yielded 8-*acetamido*-3-*hydroxy*-1 : 4-*benzisooxazine*-6-*arsinic acid* (IV).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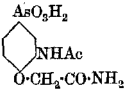
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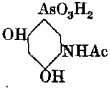

(VI.)

By using α-bromopropionyl chloride and α-bromobutyryl chloride in place of chloroacetyl chloride homologous 2-*alkylbenzisooxazines* were obtained.

2-*Acetamidophenoxyacetic acid* 4-*arsinic acid* and the corresponding *amide* (V), itself of pharmacological interest in its relationship to compounds (I) and (II), were obtained from sodium 3-acetamido-4-hydroxyphenylarsinate by the action of chloroacetic acid and chloroacetamide, respectively. Either, by the action of alkalis or mineral acids, underwent ring closure to form 3-hydroxy-1 : 4-benzisooxazine-6-arsinic acid. Similarly, 2 : 6-diacetamidophenoxyacetic acid 4-arsinic acid, on mild treatment by alkali or acid, gave

corresponding amino-derivative. Finally, 3-hydroxy-1 : 4-benzis oxazine-6-arsinic acid was obtained from 6-amino-3-hydroxy-1 : benz*iso*oxazine by the Bart reaction.

The diminution of toxicity and enhancement of curative effe in mice infected with *Trypanosoma equiperdum* shown by the ace amido-derivative (IV), when administered orally or intravenousl as compared with the parent substance (III) (Ewins and Everet *Brit. J. Venereal Diseases*, 1927, **3**, 1; 1928, **4**, 181) made it desirat to prepare a number of other 8-derivatives and also some of i eleven structural isomerides.

Attempts to prepare the 8-hydroxy-derivative have, howeve proved unsuccessful. None could be isolated by the therm decomposition of the diazo-derivative of 8-amino-3-hydroxy-1 : benz*iso*oxazine-6-arsinic acid, nor could 3 : 4-dihydroxyphenylarsir acid or its 5-nitro- or 5-amino-derivative be synthesised as a startii point for ring formation (compare Fargher, J., 1920, **117**, 865).

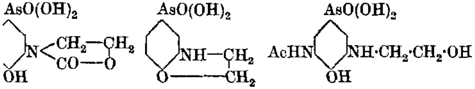
5-Acetamido-2 : 4-dihydroxyphenylarsinic acid (VI) and the corr sponding *3 : 7-dihydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid* were al prepared for comparison from 5-nitro-2 : 4-dihydroxyphenylarsin acid (Bauer, *Ber.*, 1915, **48**, 515).

The nitration of 3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic ac gave a mixture of *5-nitro-, 7-nitro-*, and *8-nitro-3-hydroxy-1 : benz*iso*oxazine-6-arsinic acids*. The last was present in 1—3% yie only and was better prepared from 5-nitro-3-amino-4-hydrox phenylarsinic acid by the chloroacetyl chloride method. The pr portion of the 5- and 7-nitro-compounds varied with the tempe ature of nitration. The 5-isomeride, the formation of which favoured by low temperature, is the more soluble in water ar may be separated by repeated fractional crystallisation, but best separated by means of its neutral di-ammonium salt. Redu tion of each by the method of Jacobs, Heidelberger, and Rc (*J. Amer. Chem. Soc.*, 1918, **40**, 1580) gave the correspondir amino-compounds, the behaviour of which with nitrous acid ga the clue to their orientation: *5-amino-3-hydroxy-1 : 4-benz*iso*oxazin 6-arsinic acid* gave an insoluble *triazole* (compare 5-amino-3-hydrox 1 : 4-benz*iso*oxazine; preceding paper) and the *7-amino*-compoun gave a diazo-compound which coupled normally with alkali β-naphthol, etc. This conclusion was fully confirmed by d arsenication of the amino-compounds, 5-amino-3-hydroxy-1 : benz*iso*oxazine-6-arsinic acid giving with boiling 5*N*-hydrochlo acid a quantitative yield of 5-amino-3-hydroxy-1 : 4-benz*iso*oxazir The 7-amino-derivative, treated similarly, gave a small yield of

lphite solution, it de-arsenicated smoothly with the formation in od yield of 7-amino-3-hydroxy-1 : 4-benz*iso*oxazine.

Attempts to prepare 2 : 3-*dihydro*-1 : 4-*benzisooxazine-6-arsinic id* (VIII) by the action of ethylene chlorohydrin on 3-amino-hydroxyphenylarsinic acid with the intermediate formation of 3-hydroxyethylamino-4-hydroxyphenylarsinic acid were unsuccessful, but the application of the method of Adams and Segur . *Amer. Chem. Soc.*, 1923, **45**, 785) led to fair yields of the cyclic id.

The action of β-chloroethyl chlorocarbonate on sodium 3-amino-ıydroxyphenylarsinate gave 3-ω-*chlorocarbethoxyamino-4-hydroxy-enylarsinic acid*, which, with caustic soda, gave the required acid. is assumed that there is formed as an intermediate product hydroxy-2-keto-3-phenyl-4 : 5-dihydro-1 : 3-*iso*oxazole-5′-arsinic id (VII).



(VII.) (VIII.) (IX.)

e mechanism by which this loses carbon dioxide to form the d (VIII) is obscure, especially since attempts to form 8-acet-ido-2 : 3-dihydro-1 : 4-benz*iso*oxazine-6-arsinic acid by an analous method led to the formation of 5-acetamido-3-β-hydroxyethylino-4-hydroxyphenylarsinic acid (IX), which was isolated as the responding *arseno*-compound readily soluble in caustic alkalis. this case, therefore, ring closure does not occur.

In the 3-hydroxy-1 : 4-benz*iso*oxazine-8-arsinic acid series, the *rent* substance was obtained from 3-amino-2-hydroxyphenylarsinic d by the chloroacetyl chloride method and also from 8-amino-ıydroxy-1 : 4-benz*iso*oxazine by the Bart method. Its amino-rivative was obtained similarly from 3-amino-5-acetamido-2-droxyphenylarsinic acid and also from 3 : 5-diamino-2-hydroxy-enylarsinic acid (King, J., 1927, 1050) by chloroacetylation in aline solution.

EXPERIMENTAL.

A. 3-*Hydroxy*-1 : 4-*benzisooxazine-5-arsinic Acid.*

2-Nitro-3-hydroxyphenylarsinic acid was prepared almost as cribed in D.R.-P. 256343 (1913). The 2-nitro-3-carbethoxy-

It formed rich yellow, hexagonal plates, m. p.* 208° (decomp.) (Found : As, 28·5 ; N, 5·3. Calc. : As, 28·5 ; N, 5·3%).

2-Amino-3-hydroxyphenylarsinic acid (compare Fourneau, Tréfouel, and Bénoit, *Bull. Soc. chim.*, 1927, **41**, 499) was obtained in 52% yield by reducing the above nitrohydroxy-acid (55 g. in 330 c.c. of hot water and 58 g. of sodium hydroxide) with glucose (44 g.). The mixture was gently boiled for 5 minutes and, after 1 hour, acidified markedly to Congo-red. Treatment with charcoal, filtration, and neutralisation to Congo-red with 10*N*-sodium hydroxide gave the amino-compound, which, after purification (compare Christiansen, *J. Amer. Chem. Soc.*, 1920, **42**, 2403), formed characteristic wedge-shaped crystals (Found : As, 32·2 ; N, 5·9. Calc. : As, 32·2 ; N, 6·0%). The calcium salt formed hexagonal plates and the acetyl derivative rectangular plates, m. p. 207—210° (decomp.) (Found : As, 27·4. Calc. : As, 27·3%).

3-*Hydroxy*-1 : 4-*benzisooxazine*-5-*arsinic Acid*.—2-Amino-3-hydroxyphenylarsinic acid (20 g.), dissolved in 2*N*-sodium hydroxide (50 c.c.), was treated alternately with chloroacetyl chloride (15 c.c. in all) and 25% sodium hydroxide solution at 50°. The mixture was made strongly alkaline and heated at 90° for 10 minutes, more alkali being added as acidity developed. The cyclic *arsinic acid*, obtained in 60% yield on acidification, crystallised from boiling water in colourless rhombs, m. p. 245—248° (decomp.) (Found : As, 27·5 ; N, 5·0. $C_8H_8O_5NAs$ requires As, 27·5 ; N, 5·1%). The calcium, barium, and magnesium salts were amorphous, white solids The orientations of this compound and of 2-nitro-3-carbethoxyaminophenylarsinic acid were confirmed by reduction of the latter by glucose and alkali giving 2 : 3-diaminophenylarsinic acid, m. p 198° (decomp.) (compare D.R.-P. 256343).

B. 3-*Hydroxy*-1 : 4-*benzisooxazine*-6-*arsinic Acid and its Derivatives*.

Preparation of the Acid.—(a) 2-Nitrophenoxyacetic acid 4-arsinic acid (Christiansen, *J. Amer. Chem. Soc.*, 1922, **44**, 2339), reduced by ferrous hydroxide (Jacobs, Heidelberger, and Rolf, *loc. cit.*) gave the *acid* in 57% yield. It crystallised from boiling water in rhombs, not molten at 300°, and was insoluble in cold water, dilute hydrochloric acid, and the usual organic solvents but soluble in alkalis and alkali carbonates (Found : As, 27·3 ; N, 5·25%). The calcium salt formed rosettes of needles, but the magnesium salt was amorphous.

(b) 2-*Acetamidophenoxyacetic acid* 4-*arsinic acid*. To 3-acetamido

4-hydroxyphenylarsinic acid (45·5 g.) suspended in water (110 c.c.), sodium hydroxide (20 g.) in water (20 c.c.), followed by chloroacetic acid (16 g.), was added and the mixture was refluxed until it was acid to litmus (¾ hour). A further 7 g. of sodium hydroxide in water (7 c.c.) and chloroacetic acid (8 g.) were added and the boiling was continued until acidity to litmus again developed; the mixture was then acidified to Congo-red and, after cooling, the *arsinic acid* collected. After purification by solution in alkali, addition of acetic acid, filtration from a small amount of unchanged material, and acidification of the filtrate to Congo-red, it crystallised in long pointed needles, not molten at 280° (yield, 66%) (Found: As, 22·5; N, 4·15. $C_{10}H_{12}O_7NAs$ requires As, 22·5; N, 4·2%). The magnesium salt was amorphous.

2-*Acetamidophenoxyacetamide* 4-*arsinic acid* was prepared (yield, 26 g.) in a somewhat similar manner from 3-acetamido-4-hydroxyphenylarsinic acid (27·5 g.) and chloroacetamide (15 + 10 + 5 g.), sodium bicarbonate being added as the alkaline reaction disappeared. It crystallised from water in colourless, hexagonal plates, m. p. 236° (decomp.) (Found: As, 22·3; N, 8·15. $C_{10}H_{13}O_6N_2As$ requires As, 22·6; N, 8·4%) and formed an insoluble amorphous magnesium salt.

2-Acetamidophenoxyacetic acid 4-arsinic acid was heated (10 g.) for 1 hour at 90° with 5*N*-sodium hydroxide (20 c.c.) or refluxed (2 g.) with 4*N*-hydrochloric acid (10 c.c.). On acidification in the former case and on cooling in the latter, 3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid was obtained (yields, 5·5 g. and 1 g., respectively) (Found: As, 27·3; N, 5·0%). The corresponding amide hydrolysed similarly.

(c) 6-Amino-3-hydroxy-1 : 4-benz*iso*oxazine hydrochloride (20 g.) (Newbery and Phillips, preceding paper), dissolved in water (200 c.c.) and hydrochloric acid (20 c.c.; *d* 1·12), was diazotised at 0—5° by sodium nitrite (7 g.) in solution and slowly added to a suspension of copper arsenite (prepared from arsenious oxide, 15 g., water, 40 c.c., sodium hydroxide, 6 g., and copper sulphate, 1·5 g.). The reaction of the mixture was maintained slightly alkaline by the addition of further sodium hydroxide when necessary. After heating with charcoal at 80°, the liquid was filtered, acidified to litmus, filtered from amorphous material after standing for some time, and acidified to Congo-red; the arsinic acid (12·5 g.; 46%) was then precipitated (Found: As, 27·3%).

(d) 3-Chloroacetamido-4-hydroxyphenylarsinic acid (1 g., m. p. 240°) prepared by a modification of Raiziss and Fisher's method

ıe same cyclic arsinic acid (0·6 g.) was obtained (Found: As 7·5%).

(e) The cyclic acid (Found: As, 27·4; N, 5·1%) was also obtained irectly from 3-amino-4-hydroxyphenylarsinic acid as described ıder 3-hydroxy-1 : 4-benz*iso*oxazine-5-arsinic acid.

2-Nitrophenoxyacetic Acid 4-*Dichloroarsine*.—A solution of 2-nitro- ıenoxyacetic acid 4-arsinic acid (10 g.) in water (10 c.c.) and ydrochloric acid (*d* 1·16; 25 c.c.) was added to a solution of ›tassium iodide (0·5 g. in 20 c.c. of water) saturated at 10° with lphur dioxide. This gas was passed into the mixture at 10° for hour and an equal volume of hydrochloric acid was then added. ıe *dichloroarsine* (7·2 g.; 70%), precipitated as rosettes of plates as washed with hydrochloric acid and dried in a vacuum over dium hydroxide. This compound (Found: As, 21·7; N, 4·2 , 20·2. $C_8H_6O_5NCl_2As$ requires As, 21·9; N, 4·1; Cl, 20·75%) very resistant to aqueous hydrolysis, and attempts to reduce it stannous chloride or sodium hyposulphite were unsuccessful. ›rrous hydroxide, however, gave a small yield of 3-hydroxy-1 : 4- ›nz*iso*oxazine 6-arsenoxide which could not be purified.

3-Hydroxy-1 : 4-*benzisooxazine* 6-*Arsenoxide*.—Reduction of the ›rresponding arsinic acid as described above under 2-nitrophenoxy ›etic acid 6-dichloroarsine gave a 60% yield of 3-hydroxy-1 : 4 ›nz*iso*oxazine 4-dichloroarsine. This resisted purification, but gave ı solution in 2*N*-sodium hydroxide and addition of hydrochloric ›id until the solution was only faintly acid to Congo-red, the *senoxide* in sphæro-crystals, insoluble in water or dilute mineral ›ids, alkali carbonates or dilute ammonia, but readily soluble in ›cess of dilute caustic alkali solution (Found: As, 31·3; N, 5·85 $_8H_6O_3NAs$ requires As, 31·4; N, 5·85%). On treatment with ›cess of hydrochloric acid the dichloroarsine was obtained.

3 : 3′-*Dihydroxy*-6 : 6′-*arseno*-1 : 4-*benzisooxazine*.—3-Hydroxy-1:4 ›nz*iso*oxazine-6-arsinic acid (2·7 g.), dissolved in water (20 c.c. ›d saturated sodium carbonate solution (5 c.c.), was added to ›ld solution of magnesium chloride hexahydrate (2 g.) and sodium yposulphite (10 g.) in water (200 c.c.). The filtered solution, on ›ating at 50—60° for 1½ hours, gave the *arseno*-compound, which ›ter being washed with water and dried in a vacuum over sulphuric ›id, was a light yellow, amorphous solid, insoluble in water, dilute ›ineral acids, alkalis, and the ordinary organic solvents (Found s, 33·2; N, 6·4. $C_{16}H_{12}O_4N_2As_2$ requires As, 33·6; N, 6·3%).

Nitration of 3-Hydroxy-1 : 4-benzisooxazine-6-arsinic Acid.—The ›sinic acid (20 g.), intimately mixed with potassium nitrate (7·5 g.) [illegible] ... thre

itro-compounds were recrystallised from hot water (500 c.c.), aving first been dissolved by the aid of a little sodium hydroxide, ollowed by acidification. The treatment of the liquors is described elow under the 8-nitro-derivative. The recrystallised solid was uspended in water (40 c.c.), and 15% ammonia added until a faint mell of ammonia and a faintly alkaline reaction were produced. he ammonium salt precipitated was collected and washed with a ttle ice-water; on acidification of its solution in boiling water 100 c.c.), 7-nitro-3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid was btained. The liquor, which contained a di-ammonium salt, on cidification gave 5-nitro-3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic cid. The following table indicates the relative yields of the 7- nd 5-nitro-isomerides.

Temp. of nitration.	Total yield.	7-Isomeride.	5-Isomeride.
0°	72%	29%	39%
10	75	35	35
30	73	41	28

5-*Nitro*-3-*hydroxy*-1 : 4-*benz*iso*oxazine*-6-*arsinic acid* crystallises om water in yellow prisms (Found: As, 23·7. $C_8H_7O_7N_2As$ equires As, 23·6%). It forms soluble crystalline calcium, barium, nd magnesium salts and a sparingly soluble mono-ammonium salt. n reduction with ferrous hydroxide the corresponding *amino*-ompound was obtained in 70% yield (Found: As, 26·1; N, 9·7. $_8H_9O_5N_2As$ requires As, 26·0; N, 9·7%). It crystallises from ater in colourless prisms, changing to hexagonal plates, not molten t 300°, is soluble in excess of mineral acids, but is reprecipitated n addition of water. The calcium and barium salts crystallise in hite needles, the magnesium salt is micro-crystalline. The sodium lt is sparingly soluble in water but readily soluble in excess of austic alkali. Attempts to acetylate this arsinic acid in alkaline acetic acid solution or by the action of acetic anhydride were nsuccessful, the unchanged arsinic acid being obtained in the first vo cases. The *triazole* formed white, hexagonal tufts or prisms, . p. 247° (decomp.), from boiling water (Found: As, 23·7; N, 2·9. $C_8H_6O_5N_3As,H_2O$ requires As, 23·7; N, 13·25%). The lcium, barium, and magnesium salts were all sparingly soluble, norphous, white solids, the calcium salt being less soluble in oiling than in cold water.

De-arsenication of 5-*amino*-3-*hydroxy*-1 : 4-*benzisooxazine*-6-*arsinic* *id.* The amino-arsinic acid (10 g.) was refluxed for 1 hour with N-hydrochloric acid (50 c.c.). The filtered solution on cooling ... 5·2 g. of 5-amino-3-hydroxy-1 : 4-benzisooxazine hydrochloride.

sodium carbonate and reconversion of the crude base (total yie 90%). The hydrochloride gave with sodium acetate 5-amino hydroxy-1 : 4-benz*iso*oxazine, m. p. 236° (not depressed by adm ture with the synthetic base; preceding paper).

*7-Nitro-3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid* crystalli from boiling water, in which it was sparingly soluble, in lo yellow prisms (Found: As, 24·0%). The calcium, barium, a magnesium salts are soluble yellow solids. On reduction w ferrous hydroxide or glucose and alkali it gave a 70% yield *7-amino-3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid*, which form white prisms, m. p. 258—260° (decomp.), on addition of water its solution in 25% sulphuric acid (Found: As, 26·0; N, 9·5% The barium and calcium salts are crystalline (needles), the magnesi salt is amorphous. The *acetyl* derivative crystallised in wh prisms, decomp. 275° (Found: As, 22·8; N, 8·5. $C_{10}H_{11}O_6N_2$ requires As, 22·7; N, 8·5%), and the *urethane* in long need (Found: As, 21·1; N, 7·7. $C_{11}H_{13}O_7N_2As$ requires As, 20·9; 7·8%). Both form amorphous calcium and magnesium salts.

*De-arsenication of 7-amino-3-hydroxy-1 : 4-benz*iso*oxazine-6-arsi acid.* The amino-arsinic acid (5 g.) was boiled under reflux wi sodium bisulphite (3 g.) in water (20 c.c.). Solution was quick effected and 7-amino-3-hydroxy-1 : 4-benz*iso*oxazine began separate. After 30 minutes the mixture was made alkaline wi sodium carbonate. The product (2·5 g.; 85%) crystallised fr water in colourless prisms, m. p. 220°, not depressed by admixtu with synthetic 7-amino-3-hydroxy-1 : 4-benz*iso*oxazine (precedi paper).

*3 : 7-Dihydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid*, obtained good yield from 5-amino-2 : 4-dihydroxyphenylarsinic acid (Bau *loc. cit.*) by chloroacetylation in alkaline solution, crystallised fr boiling water in white plates, not molten at 300° (Found: 26·1; N, 4·9. $C_8H_8O_6NAs$ requires As, 26·0; N, 4·9%). T barium salt crystallised from boiling water in clusters of colourl prisms, the calcium and magnesium salts were amorphous.

5-Acetamido-2 : 4-dihydroxyphenylarsinic acid, obtained by acet ation of the above amino-acid in the usual way, formed colourl prisms from water (Found: As, 25·6. $C_8H_{10}O_6NAs$ requires 25·9%). The calcium and magnesium salts are amorphous.

*8-Nitro-3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic Acid.*—(a) T mother-liquors from the crystallisation of the crude nitrati product of 3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid gave, neutralisation with ammonia, addition of excess of magnesi chloride and heating, a yellow crystalline precipitate (1 ... of ...

hydrochloric acid (0·7 g. after crystallisation from boiling water) (Found: As, 23·8%).

(b) To 7·5 g. of 3-nitro-5-amino-4-hydroxyphenylarsinic acid (Newbery and Phillips, *loc. cit.*), dissolved in acetone (100 c.c.), was added chloroacetyl chloride (5 c.c.) at 25°. Removal of the bulk of solvent gave 3-*nitro-5-chloroacetamido-4-hydroxyphenylarsinic acid* (6·5 g.), which formed yellow prisms, m. p. 200° (decomp.), from boiling water (Found: As, 21·1; Cl, 9·9. $C_8H_8O_7N_2ClAs$ requires As, 21·1; Cl, 10·0%). The magnesium salt is amorphous. On treatment with slightly more than 1 mol. of sodium hydroxide a 60% yield of 8-*nitro-3-hydroxy-*1 : 4-*benz*isoo*xazine*-6-*arsinic acid*, identical with the product from (a), was obtained. It formed almost colourless prisms, decomp. 320°. The calcium salt (yellow needles) is moderately easily soluble in cold water, and the magnesium salt (yellow needles) is insoluble, differing in this respect from the magnesium salt of the 5- and 7-nitro-compounds. Attempts to prepare this acid by nitration of 2-acetamidophenoxyacetic acid 4-arsinic acid failed, unchanged material only being obtained.

2 : 6-*Diacetamidophenoxyacetic acid* 4-*arsinic acid* was obtained in 75% yield [colourless prisms, m. p. 212° (decomp.), from water] by the action of chloroacetic acid on sodium 3 : 5-diacetamido-4-hydroxyphenylarsinate (Newbery and Phillips, *loc. cit.*) as described under 2-acetamidophenoxyacetic acid 4-arsinic acid (p. 3055) (Found: As, 19·2; N, 7·1. $C_{12}H_{15}O_8N_2As$ requires As, 19·2; N, 7·2%). The magnesium salt is amorphous. On treatment with boiling 5*N*-sodium hydroxide or 5*N*-hydrochloric acid 8-*amino-3-hydroxy-*1 : 4-*benz*isoo*xazine*-6-*arsinic acid*, identical with the product obtained by reduction of the above 8-nitro-derivative with ferrous hydroxide, was obtained. It consisted of staggered plates, not molten at 300°, insoluble in water, but soluble in dilute mineral acids and in alkalis (Found: As, 26·0; N, 9·6%). The sulphate forms rhombs, sparingly soluble in cold water, the barium salt consists of colourless prisms, the calcium salt of white needles, and the magnesium salt is amorphous.

8-*Amino-3-hydroxy-*1 : 4-*benz*isoo*xazine*-6-*hydroxychloroarsine hydrochloride* was obtained in 90% yield by reduction of the above amino-arsinic acid in 5*N*-hydrochloric acid by sulphur dioxide and potassium iodide, followed by precipitation with excess of hydrochloric acid (*d* 1·16). It formed tiny rhombs or needles (Found: As, 23·0; N, 8·1; Cl, 22·0. $C_8H_8O_3N_2ClAs,HCl$ requires As, 22·9; N, 8·6; Cl, 21·7%) and gave on treatment with water 8-*amino-3-hydroxy-*1 : 4-*benzisooxazine-6-arsenoxide hydrochloride*, which crystallised in

8 : 8'-*Diamino*-3 : 3'-*dihydroxy*-6 : 6'-*arseno*-1 : 4-*benz*isoo*xazine* w obtained as a pale yellow, amorphous solid, insoluble in wat dilute caustic alkali solutions, and organic solvents, soluble dilute hydrochloric acid (Found: As, 30·5; N, 11·7; atomic ra As : N = 1 : 2·06. $C_{16}H_{14}O_4N_4As_2$ requires As, 31·5; N, 11·8%

8-*Acetamido*-3-*hydroxy*-1 : 4-*benz*isoo*xazine*-6-*arsinic acid*, ma either by acetylation of the corresponding amino-acid or by chlo acetylation in alkaline solution of 3-amino-5-acetamido-4-hydro phenylarsinic acid (Newbery and Phillips, *loc. cit.*), formed colourl prisms, m. p. 275—280° (decomp.) (Found: As, 22·7; N, 8·5% The barium and magnesium salts are amorphous. On reducti with sulphur dioxide and potassium iodide as above describ 8-*acetamido*-3-*hydroxy*-1 : 4-*benz*isoo*xazine*-6-*dichloroarsine* (tufts white needles) was obtained; this on treatment with water ga the *arsenoxide*, clusters of white needles, insoluble in water, sodiu carbonate, or dilute mineral acids, soluble in dilute sodium hydroxi solution and in excess only of 10*N*-ammonia (Found: As, 25· N, 9·4. $C_{10}H_9O_4N_2As$ requires As, 25·3; N, 9·5%).

8 : 8'-*Diacetamido*-3 : 3'-*dihydroxy*-6 : 6'-*arseno*-1 : 4-*benz*isoo*xazi* was obtained as a yellow amorphous solid, stable in air and insolul in water, dilute mineral acids, alkalis, and organic solvents (Foun As, 26·1. $C_{20}H_{18}O_6N_4As_2$ requires As, 26·8%).

3-*Hydroxy*-1 : 4-*benz*isoo*xazine*-6-*arsinic Acid* 8-*Glycineamide*.—T 8-amino-3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid (13 g.) sodium carbonate solution was gradually added, during 1 hou chloroacetamide (5 g.) alternately with sodium bicarbonate (5 g a faint alkalinity to litmus being maintained. On acidification Congo-red, the *arsinic acid* was obtained in 60% yield. It form hexagonal plates from boiling water (Found: As, 21·5; N, 12·0 $C_{10}H_{12}O_6N_3As$ requires As, 21·7; N, 12·2%).

8-*Glycylamino*-3-*hydroxy*-1 : 4-*benz*isoo*xazine*-6-*arsinic Acid*.— Amino-3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid (20 g.) in 2*N* sodium hydroxide was treated with chloroacetyl chloride (10 c.c and 2*N*-sodium hydroxide by the Schotten–Baumann method. C acidification 8-chloroacetamido-3-hydroxy-1 : 4-benz*iso*oxazine- arsinic acid was precipitated, which, after filtration and washi with water, was dissolved in excess of ammonia (*d* 0·880). Aft several hours, the mixture was heated to drive off the excess ammonia and acidified strongly to Congo. Addition of sodiu acetate to the filtered solution gave the *glycyl* derivative. Purifi by solution in hydrochloric acid and neutralisation with sodiu acetate, it formed minute needles, soluble in mineral acids and alkalis (Found: As, 21·5. $C_{10}H_{12}O_6N_3As$ requires As, 21·7%).

8-*Chloro*-3-*hydroxy*-1 : 4-*benz*isoo*xazine*-6-*arsinic Acid*.—8-Amin

3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid (28 g.) was diazotised at 0°, and the diazo-compound was collected and boiled with cuprous chloride (15 g.) dissolved in saturated sodium chloride solution containing a little hydrochloric acid. After treatment with charcoal and cooling, the precipitate obtained (15 g.; 50%) was dissolved in warm alkali and reprecipitated by acid; it then formed yellow prisms, not molten at 280°, sparingly soluble in boiling water (Found: As, 24·1; N, 4·3; Cl, 11·4. $C_8H_7O_5NClAs$ requires As, 24·4; N, 4·6; Cl, 11·5%). The magnesium salt is amorphous.

*3-Hydroxy-8-methyl-*1 : 4-*benzisooxazine-*6-*arsinic Acid.—The arsination of* o-*cresol.* The method of Christiansen (*J. Amer. Chem. Soc.*, 1923, **45**, 801) for the preparation of 4-hydroxy-3-methylphenylarsinic acid was modified by preliminary distillation of the *o*-cresol–arsenic acid mixture until ½ molecule of water had been removed. The residual mixture was then refluxed with mechanical agitation for 4 hours and worked up as suggested by Christiansen. In this way a 25% yield of sodium 4-hydroxy-3-methylphenylarsinate, *i.e.*, twice that recorded by Christiansen, was obtained.

The sodium salt on nitration (compare Benda and Bertheim, *Ber.* 1911, **44**, 3450) gave 3-nitro-4-hydroxy-5-methylphenylarsinic acid in 70% yield. On reduction by glucose and alkali as described under 2-amino-3-hydroxyphenylarsinic acid (p. 3054), a 60% yield of the corresponding amino-acid was obtained (compare D.R.-P 224,953; Fourneau, *Ann. Inst. Pasteur*, 1926, 944). Purified by solution in hydrochloric acid and reprecipitation by sodium acetate it formed colourless prisms, insoluble in water but readily soluble in alkalis. The monosodium salt (white needles) is sparingly soluble in cold water.

3 : 3′-*Diacetamido-*4 : 4′-*dihydroxy-*5 : 5′-*dimethylarsenobenzene*, obtained by reduction of 3-acetamido-4-hydroxy-5-methylphenylarsinic acid (compare E.P. 254,086), was a yellow, amorphous solid insoluble in water, mineral acids, and organic solvents, soluble in dilute sodium hydroxide solution and in 50% acetic acid (Found As, 29·8; N, 6·0. $C_{18}H_{20}O_4N_2As_2$ requires As, 31·4; N, 5·9%).

3-*Hydroxy-8-methyl-*1 : 4-*benzisooxazine-*6-*arsinic acid*, made by chloroacetylation in alkaline solution of 3-amino-4-hydroxy-5-methylphenylarsinic acid, crystallised from water in white prisms soluble in alkalis (Found: As, 25·9; N, 4·4. $C_9H_{10}O_5NAs$ requires As, 26·2; N, 4·9%).

3 : 3′-*Dihydroxy-*8 : 8′-*dimethyl-*6 : 6′-*arseno-*1 : 4-*benzisooxazine* was obtained as a yellow, amorphous solid insoluble in water, dilute mineral acids, alkali, and organic solvents, but soluble in 50% acetic acid (Found: As, 30·6; N, 5·6. C_{18}

8-β-Hydroxyethylamino-3-hydroxy-1 : 4-benzisooxazine-6-arsinic Acid.—8-Amino-3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid (15 g.) was treated at 40—50° with β-chloroethyl chlorocarbonate (10 c.c.) and 10*N*-sodium hydroxide. On acidification, 8-ω-chlorocarbethoxyamino-3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid (compare 3-ω-chlorocarbethoxyamino-4-hydroxyphenylarsinic acid, below) separated; it formed white needles from 50% acetic acid. This compound (12 g.) was refluxed for 40 minutes with 5*N*-sodium hydroxide (60 c.c.); on acidification, carbon dioxide was liberated and *8-β-hydroxyethylamino-3-hydroxy-1 : 4-benzisooxazine-6-arsinic acid* (white prisms from boiling water) separated (Found : As 22·5; N, 8·4. $C_{10}H_{13}O_6N_2As$ requires As, 22·5; N, 8·4%).

3-Hydroxy-8-carboxy-1:4-benzisooxazine-6-arsinic Acid.—5-Aminosalicylic acid (made by the method of Armin, Fisher, and Rosenberg, *Ber.*, 1898, **31**, 81) gave, by a modification of the Bart method, a 40% yield of 4-hydroxy-3-carboxyphenylarsinic acid.

3-Nitro-4-hydroxy-5-carboxyphenylarsinic acid (16 g.) separated when a mixture of 4-hydroxy-3-carboxyphenylarsinic acid (20 g.) and potassium nitrate (7·7 g.), added to sulphuric acid (100 c.c.) at 5°, was poured into ice-water (500 c.c.). It formed rich yellow plates of a monohydrate from boiling water and melted at 282—284° (decomp.) when anhydrous. It is moderately easily soluble in cold water and readily soluble in alkalis, giving a deep red solution with excess of sodium hydroxide (Found: H_2O, 5·7; As, 22·8; N, 4·25. $C_7H_6O_8NAs,H_2O$ requires H_2O, 5·5; As, 23·1; N, 4·3%). The magnesium, barium, and calcium salts are amorphous. On reduction with glucose and alkali, *3-amino-4-hydroxy-5-carboxyphenylarsinic acid* was obtained; it formed white rhombs, not molten at 300°, from water (Found : As, 27·0; N, 4·8. $C_7H_8O_6NAs$ requires As, 27·1; N, 5·0%). The calcium, barium, and magnesium salts are amorphous. The acid is soluble in excess only of dilute mineral acids, but readily soluble in sodium hydroxide, forming a monosodium salt (needles) which is less soluble in water than the disodium salt.

3-Acetamido-4-hydroxy-5-carboxyphenylarsinic acid, prepared from the above amino-acid by acetylation in alkaline solution, crystallised from boiling water in long, colourless needles, m. p. 250—254° (decomp.). The magnesium and calcium salts are amorphous (Found: As, 23·4; N, 4·6. $C_9H_{10}O_7NAs$ requires As, 23·5; N, 4·4%).

3-Hydroxy-8-carboxy-1 : 4-benzisooxazine-6-arsinic acid, made by chloroacetylation in alkaline solution of 3-amino-4-hydroxy-5-carboxyphenylarsinic acid, formed white rhombs, m. p. 300—305° (decomp.) from water. It was soluble in alkalis (giving neutral

solutions, but was sparingly soluble in cold water (Found: As, 23·4; N, 4·5. $C_9H_8O_7NAs$ requires As, 23·6; N, 4·4%).

3-*Hydroxy-2-methyl*-1 : 4-*benzisooxazine-6-arsinic acid* was obtained from 3-amino-4-hydroxyphenylarsinic acid as described under 3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid, α-bromopropionyl bromide being used instead of chloroacetyl chloride. It formed colourless, pointed needles, not molten at 300°, from water. The calcium salt consists of tufts of needles, and the magnesium salt is amorphous (Found: As, 26·3; N, 4·8. $C_9H_{10}O_5NAs$ requires As, 26·2; N, 4·9%).

3-*Hydroxy-2-ethyl*-1 : 4-*benzisooxazine-6-arsinic acid*, obtained similarly by means of α-bromobutyryl chloride, formed colourless needles, not molten at 280°, from water. The calcium salt consists of tiny polyhedral crystals, the *magnesium* salt is amorphous (Found: As, 25·2; N, 4·35. $C_{10}H_{12}O_5NAs$ requires As, 24·9; N, 4·65%).

8-*Acetamido-3-hydroxy-2-methyl*-1 : 4-*benzisooxazine-6-arsinic acid*, obtained from 3-amino-5-acetamido-4-hydroxyphenylarsinic acid and α-bromopropionyl bromide, formed white prisms from boiling water. It decomposes at 265° and forms an amorphous magnesium salt (Found: As, 21·7; N, 8·05. $C_{11}H_{13}O_6N_2As$ requires As, 21·8; N, 8·1%).

8-*Acetamido-3-hydroxy-2-ethyl*-1 : 4-*benzisooxazine-6-arsinic acid* formed colourless needles from boiling water (Found: As, 20·7; N, 7·9. $C_{12}H_{15}O_6N_2As$ requires As, 20·9; N, 7·8%).

3-ω-*Chlorocarbethoxyamino-4-hydroxyphenylarsinic Acid*.—To 10 g. of 3-amino-4-hydroxyphenylarsinic acid in 30 c.c. of 2*N*-sodium hydroxide at 30° were added alternately β-chloroethyl chlorocarbonate (7 c.c.) and 10*N*-sodium hydroxide, the temperature being maintained between 35° and 40° and the reaction mixture being kept alkaline to litmus but not to phenolphthalein. The filtered solution was acidified to Congo-red, and the *arsinic acid* obtained was purified by acidification of its warm solution in sodium carbonate (yield, 9·5 g.; 63%). It formed colourless rhombic crystals, m. p. 209° (decomp.), insoluble in cold water, the alcohols or in dilute mineral acids, but readily soluble in alkalis (Found: As, 22·1; N, 4·1; Cl, 10·2. $C_9H_{11}O_6NClAs$ requires As, 22·1; N, 4·1; Cl, 10·45%). The magnesium salt is amorphous.

2 : 3-*Dihydro*-1 : 4-*benzisooxazine-6-arsinic Acid*.—The above chloro-acid (9 g.) was refluxed for 15 minutes with 30 c.c. of 4*N*-sodium hydroxide. When the filtered solution was acidified to Congo-red, carbon dioxide was evolved and the required *arsinic acid* precipitated. Crystallised by acidification of its hot alkaline

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ut readily soluble in alkalis (Found: As, 29·1; N, 5·6. $C_8H_{10}O_4NAs$ equires As, 29·0; N, 5·4%). It forms a white, amorphous magnes-ım salt.

2 : 3-*Dihydro*-1 : 4-*benzisooxazine*-6-*arsenoxide* was obtained by eduction of the corresponding arsinic acid, dissolved in 7 times its weight of hydrochloric acid (*d* 1·16), with sulphur dioxide and otassium iodide as described earlier. On addition of excess of ydrochloric acid, a gum separated, which later crystallised. The rude dichloroarsine was converted into the *oxide* by treatment ith water. Purified by addition of hydrochloric acid to its solution ı sodium hydroxide, it consisted of a white, amorphous solid ısoluble in water, sodium carbonate, ammonia and organic solvents 'ound: As, 34·0. $C_8H_8O_2NAs$ requires As, 33·3%). By treat-ent with excess of hydrochloric acid the dichloroarsine was formed ı white prisms.

6 : 6′-*Arseno* (2 : 3-*dihydro*-1 : 4-*benzisooxazine*), obtained from the sinic acid by hyposulphite reduction in the normal manner, is a llow amorphous solid insoluble in water, caustic alkalis, dilute ineral acids, and the ordinary organic solvents (Found: As, 5·7; N, 6·6. $C_{16}H_{16}O_2N_2As_2$ requires As, 35·9; N, 6·7%).

3-ω-*Chlorocarbethoxyamino*-5-*acetamido*-4-*hydroxyphenylarsinic* *cid*, obtained from 3-amino-5-acetamido-4-hydroxyphenylarsinic cid by treatment with β-chloroethyl chlorocarbonate and caustic da as described under 3-ω-chlorocarbethoxyamino-4-hydroxy-henylarsinic acid, crystallised from 30% acetic acid in long needles, ı. p. 189° (decomp.). Its magnesium salt is amorphous (Found: s, 19·15; N, 7·0; Cl, 8·65. $C_{11}H_{14}O_7N_2ClAs$ requires As, 18·9; , 7·1; Cl, 8·9%).

3 : 3′-*Di*(β-*hydroxyethylamino*)-5 : 5′-*diacetamido*-4 : 4′-*dihydroxy*-*rsenobenzene*.—3-ω-Chlorocarbethoxyamino-5-acetamido-4-hydr-xyphenylarsinic acid (5 g.) was heated in the water-bath for 30 inutes with 10% sodium hydroxide solution (20 c.c.). The ixture was then cooled and added to a solution of sodium hypo-ılphite (20 g.) and magnesium chloride hexahydrate (2 g.) in water 00 c.c.). After 2 hours' heating at 55°, the *arseno*-compound as collected, washed, and dried at 90°. It is a stable, pale yellow, norphous solid, insoluble in water, sodium carbonate, dilute ydrochloric acid, or the usual organic solvents, but readily soluble . dilute caustic alkali solutions (Found: As, 26·2; N, 9·4. $_{20}H_{26}O_6N_4As_2$ requires As, 26·4; N, 9·8%).

3-nitro-2-hydroxyphenylarsinic acid (compare Fourneau, Tréfou and Bénoit, *loc. cit.*), which formed characteristic yellow nodul m. p. 252—254° (decomp.) (Found: As, 28·8%). The calciu barium, and magnesium salts were yellow, amorphous solids. (reduction as described under 2-amino-3-hydroxyphenylarsinic ac a 62% yield of 3-amino-2-hydroxyphenylarsinic acid (m. p. ov 300°; magnesium and calcium salts amorphous), was obtain (Found: As, 32·2%). 3-*Acetamido*-2-hydroxyphenylarsinic ac (compare Fourneau, etc., *loc. cit.*) forms stout plates, m. p. 20 (decomp.), from water. Its calcium salt is amorphous and barium salt microcrystalline (Found: As, 27·5; N, 5·0. Calc As, 27·3; N, 5·1%).

3-*Hydroxy*-1 : 4-*benzisooxazine*-8-*arsinic acid*, obtained either fro 3-amino-2-hydroxyphenylarsinic acid by chloroacetylation in alk ine solution as described above under the isomeric acids, or by t Bart reaction on 8-amino-3-hydroxy-1 : 4-benz*iso*oxazine (see pr vious paper), formed white needles, m. p. 298° (decomp.), fro boiling water (Found: As, 27·5; N, 5·0%). The magnesium s consists of clusters of needles, the calcium salt of characterist many-sided nodules, and the barium salt of white prisms. T *sodium salt forms white needles readily soluble in water to give* solution neutral to litmus.

6-*Amino*-3-*hydroxy*-1 : 4-*benzisooxazine*-8-*arsinic Acid.*—This w obtained in good yield from 3 : 5-diamino-2-hydroxyphenylarsi acid (King, *loc. cit.*) by chloroacetylation in alkaline soluti as in the preparation of 3-hydroxy-1 : 4-benz*iso*oxazine-5-arsir acid (p. 3054), an excess of chloroacetyl chloride being used. Pr sumably the intermediately-formed 6-chloroacetamido-3-hydrox 1 : 4-benz*iso*oxazine-8-arsinic acid is decomposed during t reaction.

6-*Amino*-3-*hydroxy*-1 : 4-*benzisooxazine*-8-*arsinic acid* (Found: A 26·0; N, 9·6%), obtained as above or by hydrolysis of the acet derivative, formed white prisms, not molten at 300°, from wat It *is insoluble in cold water and organic solvents, but readily solul* in alkalis and in dilute hydrochloric and sulphuric acids, t sparingly soluble hydrochloride (prisms) and sulphate (rhom separating on standing. The barium salt forms white prisms, a the calcium salt rhombs; the magnesium salt is amorphous microcrystalline. This acid is more basic than 7- and 5-amin 3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic acids, but less basic th 8-amino-3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid: 2·5 g. of t 6-amino-8-arsinic acid, 8-amino-6-arsinic acid, 7-amino-6-arsi acid, and 5-amino-6-arsinic acid, suspended in 10 c.c. of wat [illegible] 0·5, 4·2, 7, and 15 c.c. of 10N-sulphuric ac

for solution. Only the solutions of the last two amino-acids are hydrolysed by addition of water.

6-*Acetamido*-3-*hydroxy*-1 : 4-*benz*iso*oxazine*-8-*arsinic acid*, obtained in 80% yield by acetylation of the corresponding amino-acid or in 50% yield by chloroacetylation in alkaline solution of 3-amino-5-acetamido-2-hydroxyphenylarsinic acid (Newbery and Phillips, *loc. cit.*), consists of white needles, not molten at 300°. It is insoluble in cold, sparingly soluble in boiling water (Found: As, 22·9; N, 8·5%). The magnesium salt is a white, amorphous solid.

6 : 6′-*Diacetamido*-3 : 3′-*dihydroxy*-8 : 8′-*arseno*-1 : 4-*benz*iso*oxazine*, made by hyposulphite reduction of the above arsinic acid, is a pale yellow, amorphous solid, fairly stable in air. It is insoluble in water, alkalis, dilute mineral acids, and ordinary organic solvents (Found: As, 25·7; N, 9·5. $C_{20}H_{18}O_6N_4As_2$ requires As, 26·8; N, 10·0%).

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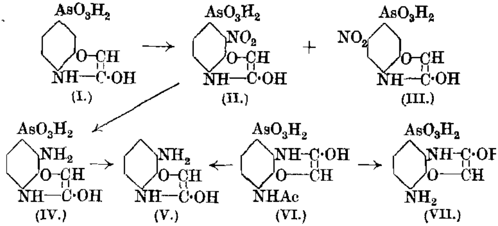
CCCCII.—*Heterocyclic Compounds containing Arsenic. Part III. Some Derivatives of* 4-*Amino*-3-*hydroxyphenylarsinic Acid.*

By Isidore Elkanah Balaban.

In Part II (preceding paper) the heterocyclic compounds described were prepared mainly from 3-amino-4-hydroxyphenylarsinic acid. Similar derivatives of 4-amino-3-hydroxyphenylarsinic acid will now be described. Ewins and Everett (*Brit. J. Venereal Diseases*, 1927, **3**, 1) have shown that 3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinic acid and its 8-acetamido-derivative have $C/T = 1/25$ and 1/80, respectively, *per os*, ratios sufficiently good to render desirable the study of further compounds of the same series.

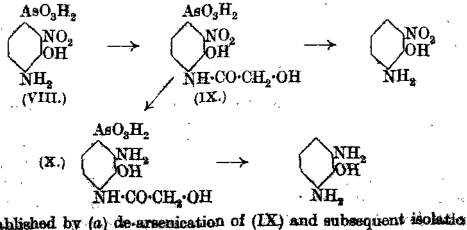
When 4-amino-3-hydroxyphenylarsinic acid is treated with chloroacetyl chloride in aqueous sodium hydroxide solution, 3-*hydroxy*-1 : 4-*benz*iso*oxazine*-7-*arsinic acid* (I) (compare Aschan, *Ber.*, 1887, **20**, 1523) is obtained. On nitration of this acid a mixture of two isomeric nitro-derivatives is obtained. These represent 8-*nitro*-3-*hydroxy*-1 : 4-*benz*iso*oxazine*-7-*arsinic acid* (II) and 6(?)-*nitro*-3-*hydroxy*-1 : 4-*benz*iso*oxazine*-7-*arsinic acid* (III), respectively, because 8-*amino*-3-*hydroxy*-1 : 4-*benz*iso*oxazine*-7-*arsinic acid* (IV), the reduction product of (II), on de-arsenication with 16% hydrochloric acid yields 8-*amino*-3-*hydroxy*-1 : 4-*benz*iso*oxazine* (V). This amine is also obtained by the acid hydrolysis of 8-*acetamido*-

3-*hydroxy*-1 : 4-*benzisooxazine*-5-*arsinic acid* (VI) (compare Benda *Ber.*, 1914, **47**, 995), which is prepared from 2-amino-4-acetamido 3-hydroxyphenylarsinic acid (Balaban, this vol., p. 809), wherea the alkaline hydrolysis proceeds normally, giving 8-*amino*-3-*hydroxy* 1 : 4-*benzisooxazine*-5-*arsinic acid* (VII).



Although (III) has not been submitted to similar treatment owin to lack of material, nevertheless it is reasonable to assume *op*-nitra tion of the benz*iso*oxazine arsinic acid under examination. Attempt to de-arsenicate the nitro-compounds by acid hydrolysis wer unsuccessful.

An unexpected result was obtained by the action of chloroacet chloride on 2-nitro-4-amino-3-hydroxyphenylarsinic acid (VIII), fo the only product isolated was 2-*nitro*-4-ω-*hydroxyacetamido*-3 *hydroxyphenylarsinic acid* (IX). This is in contrast with th behaviour of 5-*nitro*-3-*amino*-4-*hydroxyphenylarsinic acid* (Part II which gives a benz*iso*oxazine derivative normally, and it can onl be concluded that the influence of the nitro-group in this case i strong enough to inhibit ring closure. This fact was definitel



established by (*a*) de-arsenication of (IX) and subsequent isolatio of 2-nitro-6-aminophenol, and (*b*) its reduction to 2-*amino*-4-ω-*hydr oxyacetamido*-3-*hydroxyphenylarsinic acid* (X) and de-arsenicatio

the 2 : 6-diaminophenol produced being identified in the form
its di- and tri-acetyl derivatives.

When 3-nitrobenzoxazolone-5-arsinic acid, which is the n
nitration product of benzoxazolone-5-arsinic acid, was boiled v
2*N*-sodium hydroxide for 3 hours, ammonia was evolved and
only identifiable product was *5-nitro-4-amino-3-hydroxyphenylars
acid,* obtained in 41·0% yield. With hydrochloric acid, o
unchanged material was recovered.

EXPERIMENTAL.

3-Hydroxy-1 : 4-benzisooxazine-7-arsinic Acid (I).—4-Amin
hydroxyphenylarsinic acid (23·3 g.), dissolved in 2*N*-sodium hy
oxide, was treated with chloroacetyl chloride (15 c.c.); the chl
acetyl derivative which separated was redissolved by furt
additions of alkali. After heating on the water-bath for ½ hc
the solution was acidified with hydrochloric acid, 12·9 g. of
desired *acid* (yield, 47·2%) being obtained. This acid crystalli
from boiling water (10 parts) in rhomboids containing $1H_2O$, a
is identical with the compound obtained from 7-amino-3-hydro
1 : 4-benz*iso*oxazine by the Bart–Schmidt reaction (Found on a
dried material: loss at 100°, 6·2. $C_8H_{10}O_5NAs,H_2O$ requires H_2
6·2%. Found on material dried at 100°: As, 27·1; N, 4
$C_8H_{10}O_5NAs$ requires As, 27·4; N, 5·1%). It is soluble in h
alcohol and moderately easily soluble in glacial acetic acid, fr
which it crystallises in rhomboids. The calcium salt crystalli
in bunches of spikes, the magnesium and barium salts are amorpho

Nitration of 3-Hydroxy-1 : 4-benzisooxazine-7-arsinic Acid.—T
acid (10 g.) was nitrated at 0°, and on pouring the solution on
and keeping, 6·6 g. of nitro-compounds, m. p. 275° (decomp.), w
obtained. The mother-liquor deposited a further 1·8 g. (to
yield, 72·4%). After recrystallisation from water the two cr
were obtained in very pale yellow needles and colourless rectangu
plates, respectively, representing the 8-nitro- and 6(?)-nitro
hydroxy-1 : 4-benz*iso*oxazine-7-arsinic acids.

8-Nitro-3-hydroxy-1 : 4-benzisooxazine-7-arsinic acid (II) (Fou
on air-dried material: As, 23·8; N, 8·7. $C_8H_7O_7N_2As$ requi
As, 23·6; N, 8·8%) and *6(?)-nitro-3-hydroxy-1 : 4-benzisooxazi
7-arsinic acid* (III) (Found on air-dried material: As, 23·6.
8·5%) *both decompose at 280°, the latter violently.* Both ac
are sparingly soluble in glacial acetic acid, from which they cryst
lise in rods and rectangular plates, respectively, and are insolu
in alcohol. The magnesium salts are amorphous, but the calci
of the 6(?)-nitro-acid crystallises in bunches of needles a

8-*Amino*-3-*hydroxy*-1 : 4-*benz*iso*oxazine*-7-*arsinic acid* (IV), prepared from (II) by the ferrous sulphate method (yield, 66·6%), crystallised from boiling 2*N*-acetic acid (20 parts) in clusters of almost colourless, fine, silky needles containing $\frac{3}{4}H_2O$ (Found on air-dried material: loss at 100°, 4·7; As, 25·0; N, 9·2. $C_8H_9O_5N_2As,\frac{3}{4}H_2O$ requires $\frac{3}{4}H_2O$, 4·5; As, 24·9; N, 9·3%. Found on substance dried at 100°: As, 26·0. $C_8H_9O_5N_2As$ requires As, 26·0%). It is readily soluble in 2*N*-hydrochloric acid and 80% formic acid, sparingly soluble in glacial acetic acid, and insoluble in alcohol. After diazotisation it gives with sodium β-naphthoxide a bright red solution. The barium salt forms fine needles, the calcium salt is micro-crystalline, and the magnesium salt amorphous.

De-arsenication.—When the amino-acid (2 g.) just described was heated with 16% hydrochloric acid (10 c.c.) for 1 hour, the compound of m. p. 180° (see p. 3070) was obtained in 61·4% yield.

8-*Acetamido*-3-*hydroxy*-1 : 4-*benz*iso*oxazine*-7-*arsinic acid*, obtained by acetylation of the above acid in alkaline solution, crystallised from water in colourless, silky, anhydrous needles (Found on air-dried material: As, 22·6; N, 8·4. $C_{10}H_{11}O_6N_2As$ requires As, 22·7; N, 8·5%), readily soluble in 80% formic acid, almost insoluble in glacial acetic acid, and insoluble in alcohol. The magnesium salt is gelatinous and the calcium salt separates in clusters of fine needles.

2-*Nitro*-4-ω-*hydroxyacetamido*-3-*hydroxyphenylarsinic Acid* (IX).—2-Nitro-4-amino-3-hydroxyphenylarsinic acid (20 g.), chloroacetylated in the usual manner, gave 13·5 g. (yield, 59·2%) of material which crystallised from water, in which it was moderately easily soluble, in golden-brown anhydrous plates, efferv. 210° (Found: As, 22·1; N, 8·2. $C_8H_9O_8N_2As$ requires As, 22·3; N, 8·3%). The *acid* is sparingly soluble in alcohol and in glacial acetic acid, from which it crystallises in plates, and forms a rich red solution in aqueous sodium hydroxide.

De-arsenication. 0·5 G. of the nitro-acid, heated with 16% hydrochloric acid (2·5 c.c.) for ½ hour, gave 2-nitro-6-aminophenol, m. p. 110° (alone or mixed with an authentic specimen).

2-*Amino*-4-ω-*hydroxyacetamido*-3-*hydroxyphenylarsinic Acid* (X).—The corresponding nitro-acid on reduction gave the *amino-acid* (85·5% yield), which crystallised from water (20 parts) in almost colourless clusters of stout anhydrous prisms (Found: As, 25·2; N, 9·1. $C_8H_{11}O_6N_2As$ requires As, 24·5; N, 9·1%). It is soluble in excess of 2*N*-hydrochloric acid (giving a red solution after diazotisation and coupling with alkaline β-naphthol), moderately easily soluble in glacial acetic acid, very sparingly soluble in alcohol, and

De-arsenication. The product of de-arsenication gave, afte acetylation, the triacetyl derivative of 2 : 6-diaminophenol, m. p *ca.* 200°, which after treatment with alkali gave 2 : 6-diacetamido phenol, m. p. 160°.

4-ω-*Hydroxyacetamido-2-acetamido-3-hydroxyphenylarsinic acid* prepared by acetylation of the above acid, crystallised from water in which it was moderately easily soluble, in fine, colourless, silky anhydrous needles (Found on air-dried material: As, 22·0; N, 7·9 $C_{10}H_{13}O_7N_2As$ requires As, 21·7; N, 8·0%). It is moderately easil soluble in glacial acetic acid, but insoluble in alcohol. The magnes *ium salt is amorphous.*

8-*Acetamido-3-hydroxy-*1 : 4-*benzisooxazine-5-arsinic Acid*.—10·[illegible] G. of 2-amino-4-acetamido-3-hydroxyphenylarsinic acid, chloro acetylated as previously described, gave 2·95 g. (yield, 24·6%) o the *acid*, which crystallised from 2*N*-acetic acid, in which it was moderately easily soluble, in fine, colourless, silky, anhydrous needles (Found on air-dried substance: As, 23·1; N, 8·6 $C_{10}H_{11}O_6N_2As$ requires As, 22·7; N, 8·5%). It is readily soluble in 80% formic acid, moderately easily soluble in glacial acetic acid, very sparingly soluble in boiling water, and insoluble in alcohol. The magnesium salt is amorphous and the calcium salt forms acicular crystals.

8-*Amino-3-hydroxy-*1 : 4-*benzisooxazine.*—0·8 G. of the above acid was heated with 16% hydrochloric acid (4·0 c.c.) for ½ hour. On cooling, 0·5 g. of the *benzisooxazine hydrochloride* separated. It crystallises in anhydrous, stout, hexagonal prisms from water, in which it is readily soluble when hot, chars at 270°, and decomposes at *ca.* 300° (eff.). Its aqueous solution is acid to Congo-red (Found on air-dried material: Cl, 17·4; N, 14·4. $C_8H_8O_2N_2$,HCl requires Cl, 17·7; N, 14·0%). It diazotises normally. The *base* crystallises from hot water, in which it is fairly soluble, in long, colourless, silky, anhydrous needles, m. p. 180° (Found on air-dried material: N, 16·9 $C_8H_8O_2N_2$ requires N, 17·1%). It is readily soluble in alcohol and acetone, sparingly soluble in ether, and almost insoluble in benzene. The nitrate (long rectangular prisms) and the sulphate (short stout rods) are very soluble in water. The *acetyl derivative* crystallises from water, in which it is sparingly soluble, in long, colourless, silky anhydrous needles, m. p. 257° (Found on air-dried material: N, 13·6. $C_{10}H_{10}O_3N_2$ requires N, 13·6%). When the amine or its acetyl derivative is warmed with concentrated nitric and sulphuric acids, a bright blue colour develops; the amine hydrochloride produ

hydroxide (20 c.c.) for $\frac{1}{2}$ hour. This *acid* crystallises from water, which it is sparingly soluble, in long rectangular prisms whi contain $\frac{1}{2}H_2O$ not lost at 100° (Found on material dried at 100 As, 24·8; N, 9·6. $C_8H_9O_5N_2As,\frac{1}{2}H_2O$ requires As, 25·2; N, 9·4% It is readily soluble in 2*N*-hydrochloric acid and diazotises normall It is soluble in 80% formic acid, sparingly soluble in glacial acet acid, from which it crystallises in rectangular prisms, and insolub in alcohol. The magnesium salt crystallises in irregular plat the calcium and barium salts are amorphous.

Benzoxazolone-5-arsinic Acid.—4-Amino-3-hydroxyphenylarsin acid (20 g.) was dissolved in 2*N*-sodium hydroxide and treated wi carbonyl chloride; the solid which separated (yield, 20·6 g.; 93% was insoluble in hydrochloric acid and after treatment with nitro acid did not couple with sodium β-naphthoxide. This acid, me tioned in E.P. 214,628, crystallises from boiling water (25 part in long, colourless, anhydrous, boat-shaped plates (Found: As, 29· N, 5·5. Calc. for $C_7H_6O_5NAs$: As, 29·0; N, 5·4%). It is ve sparingly soluble in glacial acetic acid and alcohol, but moderate easily soluble in 80% formic acid. The magnesium salt is mic crystalline.

Nitration of Benzoxazolone-5-arsinic Acid.—The acid (8·63 g.) w nitrated at 0°, and the mixture poured on ice; 6·7 g. (yield, 66·1% of product were collected. A prolonged fractional crystallisati from water gave evidence of the presence of more than one co pound, but actually only one substance was obtained pure, the fi mother-liquor giving material which was an inseparable mixture.

3-Nitrobenzoxazolone-5-arsinic acid, the subject of U.S. 1539798, crystallises from boiling water (20 parts) in almost colo less, stout, anhydrous, quadrilateral prisms (Found on air-dri material: As, 24·8; N, 9·1. Calc. for $C_7H_5O_7N_2As$: As, 24· N, 9·2%). It is moderately easily soluble in glacial acetic a and 2*N*-acetic acid, from which it crystallises in quadrilate prisms, sparingly soluble in 80% formic acid, and almost insolu in alcohol.

5-Nitro-4-amino-3-hydroxyphenylarsinic Acid.—4 G. of the ab acid were heated with 2*N*-sodium hydroxide (40 c.c.) for 4 hou ammonia being evolved and the solution acquiring a deep reddi violet colour. On acidification the desired *acid* was obtained 41·0% yield. The mother-liquor gave with ferric chloride an inte bluish-green colour, indicating the presence of a pyrocatec derivative; only a trace of crystalline material, however, could isolated from it. This acid crystallises from water in bright yell spikes containing $1H_2O$ which is not lost at 100° (Found on mate

25·4; N, 9·4%). It is sparingly soluble in water, almost insoluble in glacial acetic acid and alcohol, soluble in formic acid and concentrated hydrochloric acid, and diazotises normally. The calcium salt separates in laminæ.

6-*Nitrobenzoxazolone-5-arsinic Acid.*—2-Nitro-4-amino-3-hydroxyphenylarsinic acid (6 g.) was treated with carbonyl chloride as previously described; the collected solid (3·9 g.; 59·6%) was insoluble in hydrochloric acid and after treatment with nitrous acid did not couple with sodium β-naphthoxide. This *acid* crystallises from water, in which it is very sparingly soluble, in long, pale brown, anhydrous, hexagonal plates (Found on material dried at 100°: As, 24·7; N, 9·2. $C_7H_5O_7N_2As$ requires As, 24·7; N, 9·2%). It is almost insoluble in alcohol and glacial acetic acid. The magnesium and barium salts are microcrystalline.

6-*Aminobenzoxazolone-5-arsinic Acid.*—The above nitro-acid on reduction gave an 82·4% yield of the *amino-acid*, which crystallised from 30 volumes of boiling water in colourless hexagonal laminæ, containing $1H_2O$ which is lost at 100° (Found on air-dried material: loss at 100°, 6·0; As, 25·8. $C_7H_7O_5N_2As,H_2O$ requires H_2O, 6·2; As, 25·7%. Found on material dried at 100°: As, 27·0; N, 10·5. $C_7H_7O_5N_2As$ requires As, 27·4; N, 10·2%). It is soluble in concentrated hydrochloric acid and diazotises normally, is readily soluble in 80% formic acid, very sparingly soluble in glacial acetic acid, and insoluble in alcohol. The magnesium, calcium, and barium salts are all microcrystalline.

6-*Acetamidobenzoxazolone-5-arsinic acid*, prepared by acetylation of the above acid, crystallised from 2*N*-acetic acid in colourless anhydrous leaflets (Found on air-dried material: As, 23·9. $C_9H_9O_6N_2As$ requires As, 23·7%). It is sparingly soluble in glacial acetic acid, from which it crystallises in minute rods. The magnesium salt is amorphous and the calcium salt microcrystalline.

6-*Acetamidobenzoxazolone-3-arsinic Acid.*—2-Amino-4-acetamido-3-hydroxyphenylarsinic acid (10 g.) was treated with carbonyl chloride as previously described. The product (9·0 g.; 81·8%) was insoluble in hydrochloric acid and after treatment with nitrous acid gave no coloration with sodium β-naphthoxide. This *acid* crystallises in anhydrous colourless leaflets from 2*N*-acetic acid, in which it is sparingly soluble (Found on air-dried material: As, 23·9; N, 8·7. $C_9H_9O_6N_2As$ requires As, 23·7; N, 8·9%). It is fairly readily soluble in water and almost insoluble in glacial acetic acid. The magnesium, calcium, and barium salts are amorphous.

and Mr. J. G. Everett, B.Sc., A.I.C., for the experimental results obtained with mice (see Ewins and Everett, *Brit. J. Venereal Diseases*, 1928, 4, 181) and also for the results detailed in the previous paper (*loc. cit.*).

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CCCCIII.—*The Chlorination of Anilides. Part V. The Significance of Velocity Measurements in Relation to the Problem of Benzene Substitution* (continued).

By ALAN EDWIN BRADFIELD and BRYNMOR JONES.

1. *The Critical Energy Increments for the Reactions of* p-*Disubstituted Benzenes.*

[N an attempt to link qualitative theories of the mechanism of ıuclear activation with the kinetic theories of reaction which have 'ound expression in the conception of the critical energy increment, ;he authors recently considered (this vol., p. 1006) the application ;o aromatic substitution reactions of the equation for reaction 7elocity $k = PSZe^{-E/RT}$ (where Z is the collision number, E the ritical increment, and S and P are probability terms depending on ;he shapes and the "phase conditions" of the molecules). Ex›ressions of the type $\log (k_o/2k_p)_{T_1} = (T_2/T_1) \log (k_o/2k_p)_{T_2}$ were leduced and employed to calculate the effect of temperature on the ›roportions of isomerides formed by further substitution of mono- .nd di-substituted benzene derivatives.* The success of our calcul- .tion warranted the provisional rejection of phase factors (P) and teric factors (S), the product of which differed for the alternative ›oints of entrance of the substituent, and justified the adoption of he hypothesis that the ratio of the isomerides formed is governed ntirely by the difference of energy of activation of the positions

* The authors regret that at the time they were completely unaware that, o long ago as 1913, in a paper of which no abstract appeared in the *Chemisches 'entralblatt*, and which appears to have been generally overlooked by those ıterested in the problem of benzene substitution (compare, *e.g.*, the disussion of the effect of temperature by Holleman, *Chem. Reviews*, 1924, 1, 21; Lapworth and Robinson, *Mem. Manchester Phil. Soc.*, 1928, 72, 43), cheffer (*Proc. K. Akad. Wetenschap. Amsterdam*, 1913, 15, 1118) had not nly deduced exactly the same expression from a thermodynamic standpoint, nd carried out a similar calculation, but had also anticipated the authors in ointing out that Holleman's empirical "product rule" implies the addition f energies of activation. They now wish to direct attention to Scheffer's

concerned. As a result of extending this hypothesis to a series of closely related ethers p-RO·C_6H_4·X, to the rate of chlorination of which relations of the type * $k_{X_1}^{OR_1}/k_{X_2}^{OR_1} = k_{X_1}^{OR_2}/k_{X_2}^{OR_2}$ apply, we were led to the conclusion that the groups already present contribute additively to the energy of activation of the position in which the new substituent will enter. By a similar treatment of velocity ratios, Hückel (*Ber.*, 1928, **61**, 1517) has recently shown, *inter alia*, that the different rates of saponification of esters of *cis*- and *trans*-isomeric substituted *cyclo*hexanols find no reasonable explanation in "steric hindrance," thus affording indirect support for our hypothesis.

According to the theory of kinetic activation, the energy condition which must be satisfied before the molecules A and B can react in a given medium is that the sum of the kinetic energies of translation, $E_A + E_B$, of the two colliding molecules should exceed E, the critical energy increment, and conclusions which appear to be of some importance may be reached by a more detailed examination of the significance of E. It is to be remembered that E is not a characteristic of either one substance or the other, but of the reaction between the two. It would seem, however, that this amount of energy E is the minimum required to bring about some essential change in the sub-atomic structure of both A and B before the molecules can become articulated to form an intermediate complex which, by a rearrangement of electronic orbits, breaks down to the new molecules C and D. A fraction, ϵ_1, then, of E represents the energy required to "activate" A, whilst ϵ_2 is required to "activate" B, there being no necessity to assume any fixed relationship between ϵ_1 and E_A, and ϵ_2 and E_B. For the reaction of A with a second reagent M, similarly

$$\epsilon_1' + \epsilon_2' = E' \gtreqless E_A + E_M$$

and again there need be no other relationship between ϵ_1' and E_A', and ϵ_2' and E_M than that expressed above. Further, there is no *a priori* reason to suppose there is any simple relationship between ϵ_1 and ϵ_1'.

The E terms for the expression for the velocity coefficients for the chlorination of p-MeO·C_6H_4·X and p-EtO·C_6H_4·X given in Part IV may now be expanded on these lines, thus :

$$\log_e(k_{p\text{-X}}^{OMe}/2Z) = -(\epsilon_{OMe} + E_{p\text{-X}} + \epsilon_{Cl_2})/RT$$
$$\log_e(k_{p\text{-X}}^{OEt}/2Z) = -(\epsilon_{OEt} + E_{p\text{-X}} + \epsilon_{Cl_2}')/RT$$

where $(\epsilon_{OMe} + E_{p\text{-X}})$ is the energy required to activate the or carbon atom, ϵ_{OMe} representing the effect of the methoxyl group, $E_{p\text{-X}}$ representing the modifying influence of the para-atom

$(\varepsilon_{OEt} + E_{p\text{-}X})$ has a similar significance. ε_{Cl_2} and ε'_{Cl_2} represent the energy required to activate the chlorine molecule for the reaction with the first and second substances respectively. The experimental work discussed in Part IV requires that (1) $E_{p\text{-}X}$ is the same in both cases, and (2) $(\varepsilon_{OMe} + \varepsilon_{Cl_2})$ and $(\varepsilon_{OEt} + \varepsilon'_{Cl_2})$ are independent of the chemical nature of X, for then

$$\log_e k_{p\text{-}X}^{OEt}/k_{p\text{-}X}^{OMe} = \{(\varepsilon_{OMe} - \varepsilon_{OEt}) + (\varepsilon_{Cl_2} - \varepsilon'_{Cl_2})\}/RT \quad . \quad . \quad (1)$$

is independent of the nature of X.

Consider now the equations for the rates of nitration of 4-ethoxyanisole in positions 2 and 3 respectively :

$$\log_e(k_2/2Z) = -(\varepsilon'_{OMe} + E_{p\text{-}OEt} + \varepsilon_{HNO_3})/RT$$
$$\log_e(k_3/2Z) = -(\varepsilon'_{OEt} + E_{p\text{-}OMe} + \varepsilon'_{HNO_3})/RT$$

where $(\varepsilon'_{OMe} + E_{p\text{-}OEt})$ is the energy required to activate carbon atom 2, ε'_{OMe} and $E_{p\text{-}OEt}$ representing respectively the effects of the methoxy- and the ethoxy-group. A similar significance attaches to ε'_{OEt} and $E_{p\text{-}OMe}$. ε_{HNO_3} and ε'_{HNO_3} are the energies required to activate the nitric acid molecule in order that it may react with carbon atoms 2 and 3 respectively. Hence

$$\log_e k_3/k_2 = \{(\varepsilon'_{OMe} - \varepsilon'_{OEt}) + (E_{p\text{-}OEt} - E_{p\text{-}OMe}) + (\varepsilon_{HNO_3} - \varepsilon'_{HNO_3})\}/RT \quad (2)$$

No theoretical grounds exist for supposing that there is any simple relation between the values $k_{p\text{-}X}^{OEt}/k_{p\text{-}X}^{OMe}$ and k_3/k_2 determined by equations (1) and (2) respectively.

The nitration in acetic acid of certain quinol ethers of the type p-RO·C_6H_4·OMe has been studied by Robinson and Smith (J., 1926, 392) and by Clarke, Robinson, and Smith (J., 1927, 2647), and the ratios k_3/k_2 have been determined. The values obtained are compared in the following table with the ratios $k_{p\text{-}X}^{OR}/k_{p\text{-}X}^{OMe}$ for the chlorination of ethers p-RO·C_6H_4·X, given in Part IV.

R.	Nitration. k_3/k_2.	Chlorination. $k_{p\text{-}X}^{OR}/k_{p\text{-}X}^{OMe}$.
Et	1·63	1·99
Pr^a	1·80	2·20
Bu^a	1·86	2·22
p-NO_2·C_6H_4·CH_2	0·38	0·143

An obvious parallelism exists, and certain simplifying assumptions will now be made in an attempt to connect equations (1) and (2).

The first assumption is that $\varepsilon_{Cl_2} = \varepsilon'_{Cl_2}$ and $\varepsilon_{HNO_3} = \varepsilon'_{HNO_3}$, and the second that in compounds of the type R_1O·C_6H_4·OR_2, the effect of RO in modifying the amount of energy required to activate carbon atom 3 is proportional to its effect on carbon atom 2, i.e.,

The third assumption is that $m(\varepsilon_{OR_1} - \varepsilon_{OR_2}) = (\varepsilon'_{OR_1} - \varepsilon_{OR_2})$ where m is a constant. Equations (1) and (2) then become

$$\log_e k_{p\cdot X}^{OEt}/k_{p\cdot X}^{OMe} = (\varepsilon_{OMe} - \varepsilon_{OEt})/RT_1 \quad . \quad . \quad . \quad (1')$$

$$\log_e k_3/k_2 = \{m(\varepsilon_{OMe} - \varepsilon_{OEt}) - mn(\varepsilon_{OMe} - \varepsilon_{OEt})\}/RT_2. \quad (2')$$

whence

$$\log_{10} k_{p\cdot X}^{OEt}/k_{p\cdot X}^{OMe} = \frac{T_2}{m(1-n)T_1}\log_{10} k_3/k_2. \quad . \quad . \quad (3)$$

Unfortunately, there is no means of determining either m or n separately, or the product $m(1 - n)$. The arbitrary value 0·6278 has been assigned to $m(1 - n)$ and the calculation of the proportions of the isomerides formed by the nitration of 4-ethoxy-, 4-propoxy-, and 4-butoxy-anisole at 0°, and of 4-*p*-nitrobenzyloxyanisole at 24° * from the data for chlorination at 20° of the ethers $RO\cdot C_6H_4\cdot X$ has been carried out by means of (3), and the results are compared with the observed values in Table I. The agreement is fairly satisfactory.

TABLE I.

Nitration of RO OMe.

R.	3-Nitro-derivative, %	
	Found.	Calc.
Et	62·2	61·4
Pr[α]	64·3	63·0
Bu[α]	65·0	63·1
p-$NO_2\cdot C_6H_4\cdot CH_2$	27·6	23·1

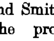
The existence of additive relationships for the critical increments for the chlorination of ethers of the type p-$RO\cdot C_6H_4\cdot X$ has been demonstrated (Bradfield and Jones, *loc. cit.*), but the above calculations would have rested on a surer foundation if it were also known that similar relationships obtain for the nitration of the ethers p-$R_1O\cdot C_6H_4\cdot OR_2$. A satisfactory kinetic method for studying nitration does not appear to have been developed, but in this particular case, static measurements, *viz.*, the determination of the final ratio of isomerides formed, can be utilised to provide a test, since Holleman's "product rule" may be applied to the data for the nitration of the two compounds p-$R_1O\cdot C_6H_4\cdot OR_3$ and p-$R_3O\cdot C_6H_4\cdot OR_2$ to calculate the ratio of the isomerides formed by

* In the experiments of Robinson and Smith, and of Clarke, Robinson, and Smith (*loc. cit.*), the temperatures were not kept rigidly constant, but these values appear to be approximately the temperatures during the nitrations. Further, the relative proportions of ether : acetic acid : nitric acid were not the same for the nitration of 4-*p*-nitrobenzyloxyanisole as for the

nitration of p-$R_1O{\cdot}C_6H_4{\cdot}OR_2$, and agreement between the observed and calculated ratios would indicate the additivity of the energies of activation. For example, from Robinson and Smith's data for 4-ethoxy- and 4-p-nitrobenzyloxy-anisole, the proportion of 2-nitro-compound formed by nitration of 4-p-nitrobenzyloxy-phenetole at 0° is calculated to be 82·2% (compare, however, footnote, p. 3076); there appear, however, to be no data available to test this calculation.

2. *Phase and Steric Factors.*

The isothermal condition $k_{X_1}^{OR_1}/k_{X_2}^{OR_1} = k_{X_1}^{OR_2}/k_{X_2}^{OR_2}$, derived from the experimental results given in Part IV, has been interpreted as indicating additivity of energies of activation for the chlorination of ethers of the type $RO{\cdot}C_6H_4{\cdot}X$, by extending to these reactions the hypothesis that the product of the phase and steric factors is constant. Nevertheless, other equally simple hypotheses would satisfy this condition, and the following analysis (for which the more detailed subdivision of the E-terms is unnecessary) indicates how some of these hypotheses may be differentiated by a measurement of the change of the ratio of the velocity coefficients with temperature.

First Hypothesis.—That the product of the phase and steric factors is the same for different substances of the type ROX, *under the same conditions, the groups* RO *and* X *then contributing additively to the energy of activation.* This is the hypothesis already promulgated. Suitable algebraic manipulation of the expressions for the velocity coefficients (given in Part IV) derived from this hypothesis, gives the relation

$$k_{X_1}^{OR_1}/k_{X_2}^{OR_2} = e^{\{(E_{X_2}-E_{X_1})+(E_{OR_2}-E_{OR_1})\}/RT}$$

whence, for two different temperatures,

$$\log\,(k_{X}^{OR_1}/k_{X_2}^{OR_2})_{T_1} = (T_2/T_1)\log(k_{X_1}^{OR_1}/k_{X_2}^{OR_2})_{T_2} \quad . \quad . \quad (4)$$

Second Hypothesis.—That the energy of activation is the same for all compounds of the type under discussion, and that a replacement of R_1 *by* R_2 *alters the product* PS *to* P′S′, *whilst a replacement of* X_1 *by* X_2 *brings about an* n*-fold increase or decrease in* PS *or* P′S′. The equations for the velocity coefficients then become

$$k_{X_1}^{OR_1} = 2PSZe^{-E/RT} \qquad k_{X_1}^{OR_2} = 2P'S'Ze^{-E/RT}$$
$$k_{X_2}^{OR_1} = 2nPSZe^{-E/RT} \qquad k_{X_2}^{OR_2} = 2nP'S'Ze^{-E/RT}$$

whence $k_{X_1}^{OR_1}/k_{X_2}^{OR_1} = 1/n = k_{X_1}^{OR_2}/k_{X_2}^{OR_2}$, as required, and

X_2 *causing an* n*-fold increase or decrease of the product* PS, *only.* The equations for the velocity coefficients become

$$k^{OR_1}_{X_1} = 2PSZe^{-E_{OR_1}/RT} \qquad k^{OR_2}_{X_1} = 2PSZe^{-E_{OR_2}/RT}$$
$$k^{OR_1}_{X_2} = 2nPSZe^{-E_{OR_1}/RT} \qquad k^{OR_2}_{X_2} = 2nPSZe^{-E_{OR_2}/RT}$$

whence $k^{OR_1}_{X_1}/k^{OR_1}_{X_2} = 1/n = k^{OR_2}_{X_1}/k^{OR_2}_{X_2}$, as required, and $nk^{OR_1}_{X_1}/k^{OR_2}_{X_2} = e^{(E_{OR_2}-E_{OR_1})/RT}$, whence

$$\log (nk^{OR_1}_{X_1}/k^{OR_2}_{X_2})_{T_1} = (T_2/T_1) \log (nk^{OR_1}_{X_1}/k^{OR_2}_{X_2})_{T_2}. \quad . \quad (6)$$

Fourth Hypothesis.—That the energy of activation is determined by the oxygen atom attached to one carbon atom, as modified by the group X, *replacement of* R_1 *by* R_2 *causing an* n*-fold increase or decrease of the product* PS *only.* The equations then become

$$k^{OR_1}_{X_1} = 2PSZe^{-(E_0+E_{X_1})/RT} \qquad k^{OR_2}_{X_1} = 2nPSZe^{-(E_0+E_{X_1})/RT}$$
$$k^{OR_1}_{X_2} = 2PSZe^{-(E_0+E_{X_2})/RT} \qquad k^{OR_2}_{X_2} = 2nPSZe^{-(E_0+E_{X_2})/RT}$$

whence $k^{OR_1}_{X_1}/k^{OR_1}_{X_2} = e^{(E_{X_2}-E_{X_1})/RT} = k^{OR_2}_{X_1}/k^{OR_2}_{X_2}$, as required, and $nk^{OR_1}_{X_1}/k^{OR_2}_{X_2} = e^{(E_{X_2}-E_{X_1})/RT}$, whence

$$\log (nk^{OR_1}_{X_1}/k^{OR_2}_{X_2})_{T_1} = (T_2/T_1) \log (nk^{OR_1}_{X_1}/k^{OR_2}_{X_2})_{T_2}. \quad . \quad (7)$$

A distinction may be drawn between these hypotheses by measuring the ratio $k^{OR_1}_{X_1}/k^{OR_2}_{X_2}$, at different temperatures, and comparing the change in the ratio with temperature with that calculated by means of expressions 4, 5, 6, and 7, respectively. The fineness of this distinction depends on the experimental accuracy, which, unfortunately, for a decisive result requires to be very much greater that is at present attainable, but Table II shows the agreement between the observed values of $k^{OMe}_{CO_2H}/k^{OEt}_{NO_2}$ at 30° and those calculated from the observed values at 20°.

TABLE II.

	$(k^{OMe}_{CO_2H}/k^{OEt}_{NO_2})_{T_1}$.	$(k^{OMe}_{CO_2H}/k^{OEt}_{NO_2})_{T_2}$. Found.	Calc.	Difference.
Hypothesis 1	74·22	68·82	64·42	−4·40
,, 1 ("corrected") ...	66·8	61·93	58·22	−3·71
,, 2	74·22	68·82	74·22	+5·40
,, 3	74·22	68·82	75·94	+7·12
,, 4	74·22	68·82	62·97	−5·85

A possible objection to the above calculation is that the data for anisic acid and for *p*-nitrophenetole, owing to experimental exigencies, do not refer to identical conditions of concentration, and the observed values of the velocity coefficients depend to some extent on the initial concentrations. However, examination of the data indicates that the velocity coefficient for anisic acid would be slightly lower if it were possible to measure it at the same concentration as that to which the data for *p*-nitrophenetole apply, and that this

" correction " would not amount to more than 10% of the value k. The value calculated by expression (4) for the ratio at 30° h been recalculated on the assumption that the " corrected " valu of the velocity coefficients at 20° and 30° are 10% lower than t observed values, and it is seen that the result is but little affect This calculation also shows that a small *systematic* error througho the measurements would lead to little difference in the result.

That the solvent is not without effect on the velocity of reacti is shown by Norrish and Smith (this vol., 129), and it is impli n all the foregoing that it affects these similar reactions to a simil extent, and that the term representing its effect, which should ntroduced into the expression for k, cancels out when ratios a taken. This assumption is in some degree justified by a calculati by Norrish and Smith's method, employing their approximatio of the ratio of the number of effective collisions to the number collisions fulfilling the energy condition for the chlorination anisic acid, p-nitrophenetole, and ω-trichloroacetanilide, and is he order 10^{-5} in each case. This factor includes, of course, a P or S terms.

Examination of Table II now shows that the first hypothesis *at least*, as correct as the others. The purpose of this discussion w have been served if it has been shown that the data considered he and in Part IV, find a quantitative explanation within the lim of experimental error, by the single assumption that the differe ates of entrance of a given substituent at different points in t ame molecule or in similar molecules under identical conditions a determined by the differences of the critical energy incremen without invoking phase or steric factors. An extensive test of t hypothesis on the lines indicated has been begun in these laboratori

3. *Structure and Reactivity.*

From the new data for the chlorination of anilides in 99% ace acid, it is seen that the value 0·580 for the velocity coefficient ω-trichloroacetanilide falls into place in the series acetanili (k = 62·2), formanilide (k = 9·2), trichloroacetanilide, showing t general parallel between the rate of chlorination of anilides of t type C_6H_5·NH·CO·R and the strength of the acid R·CO_2H. (he other hand, p-toluenesulphonanilide chlorinates even mo rapidly than benzenesulphonanilide.

The effect of replacing the imino-hydrogen atom of acetanili by a methyl group in reducing the rate of chlorination roughly one two-thousandth, is striking. An obvious explanation would

formation of a chloroamide, the former process being the slowe whilst for methylacetanilide only the direct route is availabl For reasons summarised in Part III of this series, the authors rega this explanation as unlikely, and in addition, qualitative observatio of solubility and ease of hydrolysis by aqueous acids indicate th the marked difference in properties of these two substances is n confined to speed of chlorination. *N*-Methylation of *p*-toluen sulphonanilide produces a similar but much smaller effect.

A gap in the series of alkyl groups investigated has been fill by a determination of the velocity coefficients for p-*chlorophenyl* is*butyl ether* and p-iso*butoxybenzoic acid*. The mean value of the rat $100k_{p\text{-X}}^{\text{OBu}^\beta}/k_{p\text{-X}}^{\text{OMe}} = 216$ for these ethers is of the expected order magnitude. No attempt can be made at present to conne quantitatively the reactivity of these compounds with the structure, but it is noteworthy that the results so far obtained fir a simple qualitative explanation in terms of the modern theori of benzene substitution developed by Robinson and Ingold (s summary, *Ann. Reports*, 1926 and 1927).

Experimental.

The measurements of the velocity of chlorination of the followi anilides and phenolic ethers were carried out by the method alrea described (Orton and Bradfield, J., 1927, 986; Bradfield and Jon *loc. cit.*), the medium being purified acetic acid (Orton and Bradfiel J., 1924, **125**, 960; 1927, 983) containing a total of 1 c.c. of wat per 100 c.c. of reaction mixture, previously adopted as standar Since the reproducibility of the observed velocity coefficients h been sufficiently illustrated in the earlier papers, it will suffice give in tabulated form the mean values of *k*.

Velocity Coefficients for the Chlorination of Anilides at 20°.

Concentration of chlorine = 0·0025 g.-mol./litre.
" " HCl = 0·0125 "

	Conc. of anilide (g.-mol./litre).			
	0·0025.	0·0075.	0·025.	0·075.
p-Toluenesulphonanilide	65·11	—	—	—
p-Toluenesulphonmethylanilide	2·61	2·48	2·396	—
Trichloroacetanilide	—	0·5778	0·582	—
Methylacetanilide	—	—	—	0·0338*

* Conc. of chlorine = 0·005 g.-mol./litre.

Chlorination of Trichloroacetanilide at 30°.

Anilide : chlorine : HCl = 0·0075 : 0·0025 : 0·0125 g.-mol./litre

Chlorination of iso*Butyl Ethers at* 20°.

Ether : chlorine : HCl = 0·0225 : 0·0075 : 0·0375 g.-mol./litre.
p-Chlorophenyl *iso*butyl ether, $k = 2{\cdot}701$; *p*-*iso*butoxybenzoic acid, $k = 0{\cdot}935$.

Temperature Coefficients for Ethers.

Anisic acid.

Ether : chlorine : HCl = 0·0225 : 0·0075 : 0·0375 g.-mol./litre.
$k_{30^\circ} = 0{\cdot}8898$; $k_{20^\circ} = 0{\cdot}444$; $k_{30^\circ}/k_{20^\circ} = 2{\cdot}004$.

p-Nitrophenetole.

Ether : chlorine : HCl = 0·20 : 0·02 : 0·05 g.-mol./litre.
$k_{30^\circ} = 0{\cdot}01293$; $k_{20^\circ} = 0{\cdot}005983$; $k_{30^\circ}/k_{20^\circ} = 2{\cdot}16$.

p-iso*Butoxybenzoic acid* was prepared from *p*-hydroxybenzoic acid by a modification of Ladenburg and Fitz's method for the alkylation of hydroxybenzoic acids (*Annalen*, 1867, **141**, 254): 19·4 g. (1 mol.) of *p*-hydroxybenzoic acid were dissolved in a solution of 15·8 g. (2 mols.) of potassium hydroxide in the smallest possible quantity of water, and refluxed at 120° for 7 hours with 26 g. (1·1 mols.) of *iso*butyl iodide and 2 c.c. of *iso*butyl alcohol; 10% potassium hydroxide (1 mol.) was then added, and the refluxing continued for another hour to hydrolyse any ester formed. The product was dissolved and suspended in 50 c.c. of water and just acidified with concentrated hydrochloric acid. The precipitated solid was filtered off, repeatedly washed with water until free from hydrochloric acid, and crystallised from acetic acid; m. p. 136·5° (*M*, by titration, 193·4. Calc.: *M*, 194·2).

p-*Chlorophenyl* iso*butyl ether* was prepared from *p*-chlorophenol, sodium, *iso*butyl alcohol, and *iso*butyl iodide by the usual method, and purified by distillation under 3 mm. pressure (bath temp. 95—97°). The form of the apparatus used did not permit of an accurate determination of the b. p., the velocity coefficient itself being taken as the standard of purity, as described in Part IV; $n_D^{23^\circ} = 1{\cdot}5090$ (Found: Cl, 19·4. $C_{10}H_{13}OCl$ requires Cl, 19·3%).

The authors wish to express their thanks to Prof. K. J. P. Orton F.R.S., for his continued interest and valuable advice, and to the Royal Society for a grant which partly defrayed the cost of this investigation.

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BANGOR. [*Received, October 12th*, 1928.]

CCCCIV.—*Strychnine and Brucine. Part VII. Constitution of the Alkaloids discussed in Rela to the Hypothesis that Dinitrostrychol is an Quinoline Derivative.*

By Reginald Clifford Fawcett, William Henry Perkin, ; and Robert Robinson.

In Part I (J., 1910, **97**, 305) of this investigation the chemistr strychnine and brucine was discussed from the point of view the alkaloids are at one and the same time derivatives of quin and carbazole, and when it became apparent that what we bel to have been the logical development of a structural hypotl based on these premises could not be accepted, we were comp to reconsider these fundamental assumptions.

The only thing that need be said about the question of supposed carbazole nucleus in the bases is that there is defi experimental evidence pointing to the reality of its existence that profound decompositions of strychnine do give rise to in and carbazole (compare Clemo, Perkin, and Robinson, Part IV 1927, 1589, on the formation of indole and carbazole from met strychnine); the same cannot be claimed for the hypothe quinoline residue, since no known quinoline derivative has yet l obtained by the degradation or decomposition of strychnine.

In common, we suppose, with most other chemists who l studied these problems, we have regarded the formation of din strycholcarboxylic acid by the nitration and oxidation of strych with nitric acid (Tafel, *Annalen*, 1898, **301**, 336) as a proo the existence of a quinoline ring in the alkaloid, but it is purpose of this communication to point out that the proo by no means a rigid one and that an alternative view may sustained.

Furthermore, our new suggestion that dinitrostrychol is a nitrodihydroxy*iso*quinoline has been found to be a starting p for the elaboration of new structural formulæ for strychnine brucine which are capable of symbolising the behaviour of tl bases and their derivatives in a satisfactory manner.

It is well known that strychnine contains two nitrogen atoms which one, a-N, is directly attached to an aromatic nucleus v a free para-position and also to a carbonyl group, whereas other, b-N, is not attached to an aromatic nucleus and is the m basic of the two.

Clear indications that, in methylstrychnine, the methyl group is tached to b-N are given in Part IV (*loc. cit.*).

Now it is plain that, if dinitrostrycholcarboxylic acid is a quinoline rivative, the quinoline ring nitrogen atom must be a-N, and the rtion of the molecule that includes b-N has been removed by idation; methylstrychnine, on this hypothesis, should also be idisable to dinitrostrycholcarboxylic acid.

Actually, we find that under the conditions for the production the acid from strychnine, methylstrychnine gives a different bstance (or substances) and the examination of this material, hich is not yet complete, has shown that its composition is in fair greement with the requirements of one of the formulæ

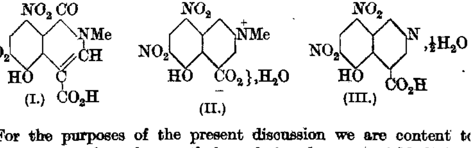
$C_{11}H_7O_8N_3$ (I), $C_{11}H_9O_8N_3$ (II), and $C_{10}H_5O_7N_3,\frac{1}{2}H_2O$ (III).

Direct estimation of the methyl attached to nitrogen gave values hich were about 30% of that anticipated from I (containing a ngle NMe group), but as the methyl iodide was liberated with ery great difficulty even at 360° it may well have happened that iere was considerable reduction to methane.

Further distillations gave quite negative results, producing no ace of methyl iodide, so that the presence of NMe in at least part of the material was qualitatively demonstrated.

The most probable constitutions corresponding to the above rmulæ are represented below and we are actively prosecuting is investigation and examining the oxidation products not only methylstrychnine, but of other *b-N*-substituted strychnines with itric acid.

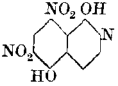
Synthetical work, in relation to the suggested formulæ, is also progress and we wish to reserve for a short time the experimenta evelopment of the subject along the lines suggested by the new onceptions which we advance in this memoir.



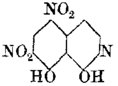
(I.) (II.) (III.)

For the purposes of the present discussion we are content to art with the fact that methylstrychnine does not yield dinitro rycholcarboxylic acid on oxidation, and we deduce from this tha e b-NMe group is not situated in the portion of the strychnin olecule that is broken up in the oxidation and that consequentl e heterocyclic nitrogen of dinitrostrychol was originally the b-N

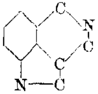
of a strychnine molecule. This is our basic assumption and we think it a sufficiently reasonable one to make it worth while to follow up the consequences. The sequel we believe to be an almost inevitable outcome of this view, but even if the latter proves to be incorrect, several of the suggestions made below can be incorporated in modified strychnine and brucine formulæ and would thus retain some value. If the ring-nitrogen of dinitrostrychol is the b-N of strychnine, then dinitrostrychol must be a dinitrodihydroxy*iso*-quinoline, since b-N cannot be attached to the aromatic nucleus.* In that case a consideration of the fate of the a-N which was attached to the benzene nucleus suggests that the place of a-N is taken by hydroxyl, and on this basis the formulæ (IV) and (V) are feasible as representations of dinitrostrychol.



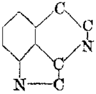
(IV.)



(V.)



(VI.)

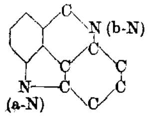


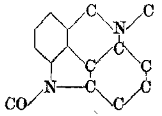
(VII.)

In view of the frequently observed degradation of strychnine to indole derivatives, (IV) and (V) point to the skeletons (VI) and (VII), respectively, as part of the strychnine molecule.

Of these (VI) seems preferable, for it allows the carbazole skeleton to be introduced in a natural manner and we arrive at the conclusion that (VIII) is a ring system of strychnine. This can be expanded to (IX) in view of the tertiary basic character of b-N and the inclusion of a-N in an acid amide grouping.

(VIII.)



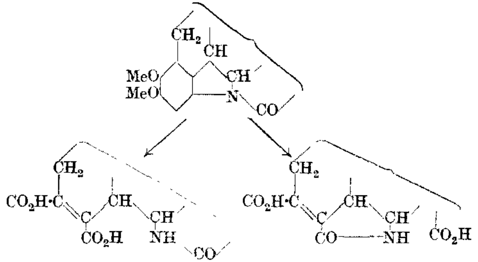


(IX.)

This hypothesis that the benzene nucleus of strychnine bears three substituents must be tested in relation to those degradations in which the benzene nucleus is broken up. No difficulties are encountered in this connexion and, for example, the degradation ch brucine to Hanssen's acid, $C_{18}H_{22}O_6N_2$, by way of kakothelin

ree p... * ...use strychnine, unlike strychnidine, does not exhibit the properties ere b-N, ...ated aromatic amine with a free para-position. ic of the t...

(nitrobruciquinone hydrate) can be expressed in full detail, the final result being given by the alternatives.



The degradation can be similarly represented if the methoxy-groups are situated in the alternative position vicinal to the indole nitrogen.

It should be mentioned at this point that the very facile nitration of strychnine to dinitrostrychnine hydrate has always appeared to us to require some special explanation.

Conceivably the formation of a phenol by rupture of the bond between the aromatic nucleus and a-N occurs at an early stage and both dinitrostrychnine hydrate and nitrobrucine hydrate may be nitrophenolic substances.

In order to make further progress it is necessary to consider the important series of degradations of strychnine and brucine that were carried out by Leuchs and his collaborators (Leuchs, *Ber.*, 1908, **41**, 1711; Leuchs and Schneider, *Ber.*, 1908, **41**, 4393; **1909**, **42**, 2494; Leuchs and Weber, *ibid.*, p. 3703; Leuchs and Reich, *Ber.*, 1910, **43**, 2417; Leuchs and Brewster, *Ber.*, 1912, **45**, 201; Leuchs and Peirce, *ibid.*, pp. 2653, 3412; Leuchs and Rauch, *Ber.*, 1914, **47**, 370; Leuchs, *ibid.*, p. 536; Leuchs and Schwaebel, *Ber.*, 1914, **47**, 1552; 1915, **48**, 1009; Leuchs and Bendixsohn, *Ber.*, 1919, **52**, 1443; Leuchs and Ritter, *ibid.*, p. 1583; Leuchs, Hellriegel, and Heering, *Ber.*, 1921, **54**, 2177; Leuchs, Grüss, and Heering, *Ber.*, 1922, **54**, 3729; Leuchs and Nitschke, *ibid.*, p. 3738; Leuchs, Gladkorn, and Hellriegel, *Ber.*, 1923, **56**, 2472).

We offer a new interpretation of these results.

On oxidation with potassium permanganate in acetone sol... brucine, $C_{23}H_{26}O_4N_2$, yields the keto-acid brucinon... C..H..O..N.. and the secondary alcoholic dihydrobrucin...

$H_{26}O_8N_2$. A stereoisomeride of the latter, namely, brucinolic d, is obtained by the reduction of brucinonic acid with sodium algam.

When brucinolic acid is heated with aqueous potassium hydroxide yields the neutral brucinolone, $C_{21}H_{22}O_5N_2$, and glycollic acid :

$$C_{23}H_{26}O_8N_2 = C_{21}H_{22}O_5N_2 + C_2H_4O_3.$$

There is no evidence that brucinonic acid is other than a monoboxylic acid, although a second carboxyl appears to be latent an *N*-CO group; moreover, the formation of *N*-CO linkages in ıte alkaline solution from >NH and $-CO_2H$ seems improbable. erefore, by far the simplest and most acceptable view of the of glycollic acid is that represented by the scheme :

$$>CH—C(O\cdot CH_2\cdot CO_2H)< \longrightarrow >C{=}C< + HO\cdot CH_2\cdot CO_2H.$$

This is supported by the facts that (1) brucinolone contains an ylene linkage not contained in brucinolic acid, and (2) the acid le *derived from dihydrobrucinonic acid decomposes with form*-ɔn of formaldehyde (Leuchs and Kanao, *Ber.*, 1924, **57**, 1318) :

$$—O\cdot CH_2\cdot CON_3 \longrightarrow >C—O\cdot CH_2\cdot NH\cdot CO\cdot OH \longrightarrow$$
$$>C—OH + CH_2O + NH_3 + CO_2.$$

need no more than this to show that strychnine and brucine tain cyclic ether oxygen and since the alkaloids also contain double bond (compare Part VI, Oxford, Perkin, and Robinson, 1927, 2389) the complete nuclear system must be elaborated n (IX) by the inclusion of three more rings.

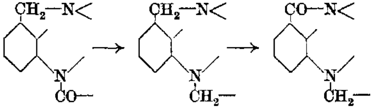
Further, since the double bond is the point of attack of the dising agent, a part of the changes involved in the formation ɔrucinonic acid must be due to the fission

$$>C—O\cdot CH_2\cdot CH{:}C< \longrightarrow >C—O\cdot CH_2\cdot CO_2H \quad CO<.$$

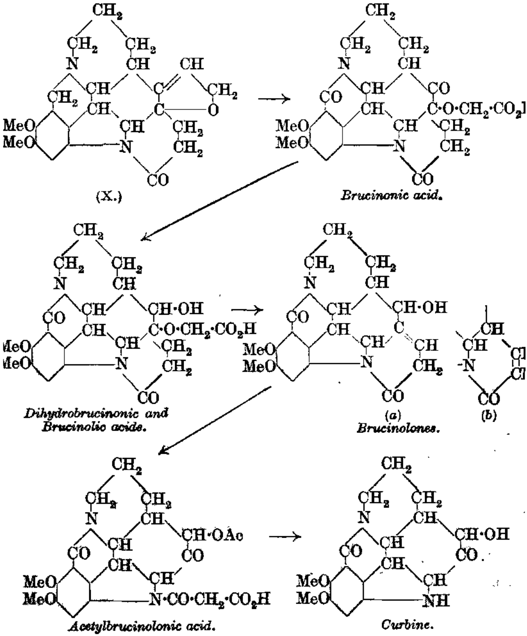
s adds 3O and in some other part of the molecule we must uiŝlıyṇd subtract 2H; it is clear that this must be due to the substi. of $-CH_2—N$ (b) into $-CO—N$ (b), because otherwise hich the ing to account for the neutral character of brucinolone. untered in erived from (IX) will include a methylene group which rucine to Hands of analogy, be readily oxidised to carbonyl, t ell known that the carbon atom numbered 1 in the b-Nyise stry inoline ring exhibits a marked susceptibility to oxidis- f the ated r

re, in the course of experiments on the reduction

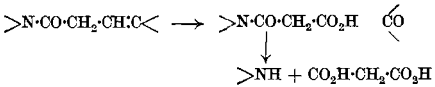
products of strychnine, a substance has been isolated which appears to be a kind of *epi*strychnine, produced in accordance with the scheme :



It is hoped that an account of this work will shortly be submitted to the Society.

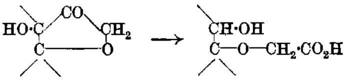


The further degradation of brucinolone to curbine has already been interpreted by Leuchs by means of the scheme :



The elaboration of (IX) so as to accommodate these results can be effected in various ways, and we have considered many alternatives; of these we prefer that, shown below, arising from the postulation of the constitution (X) for brucine.

The formation of dihydrobrucinonic acid by the direct oxidation of brucine is, on every view, a curious result; it may be due to the hydrolytic fission :



Some examples of the application of the expression (X) and the analogous strychnine formula (XI) to the explanation of the chemistry of the reduction products are represented in the annexed scheme.

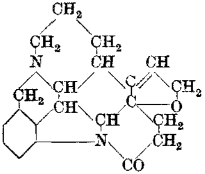
These transformations, described in Part IV (Clemo, Perkin, and Robinson, J., 1927, 1589), take a more normal course at the stage (XII) ⟶ (XIII), when the double bond in (XII) is saturated, the original ring system being reproduced.

Strychnidone (XIV) is here represented as a β-hydroxy-ketone, and the disemicarbazone described in Part IV is then in all probability a semicarbazido-semicarbazone and belongs to a recognised type of αβ-unsaturated ketone derivatives.

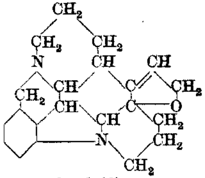
The formulæ for tetrahydrostrychnine and the products of catalytic reduction of strychnine derivatives (compare Part VI, *loc. cit.*) follow automatically, but it must be confessed that we have no very satisfactory explanation of the existence of *iso*strychnine and dihydro*iso*strychnine to put forward.

The ether oxygen appears to become hydroxylic and it is therefore possible that the formation of *iso*strychnine involves an intramolecular transfer of hydrogen and that the C–O–C group is reduced to ⋛CH HO·C⋚; perhaps the dihydroindole group provides the necessary hydrogen atoms.

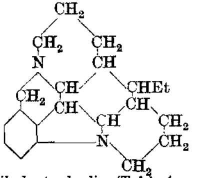
Before considering the permissible modifications of the structures



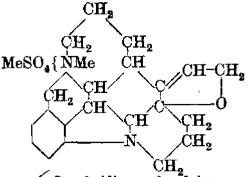
(XI.)



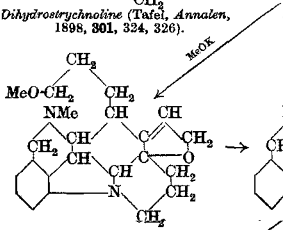
Strychnidine.



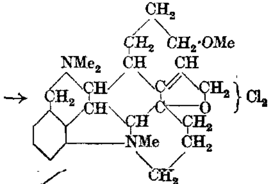
Dihydrostrychnoline (Tafel, *Annalen*, 1898, **301**, 324, 326).



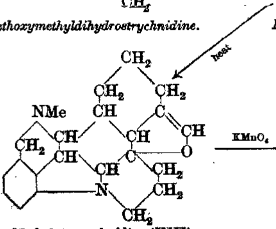
Strychnidine methosulphate.



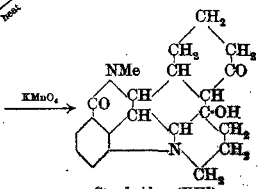
Methoxymethyldihydrostrychnidine.



Dimethochloride (XII).

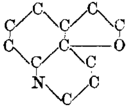


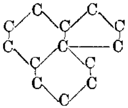
Methyl-ψ-strychnidine (XIII).



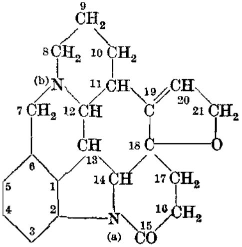
Strychnidone (XIV).

(X) and (XI) it may be noted that the assumed ring system (XV) is a heterocyclic analogue of that (XVI) occurring in cholesterol.

(XV.) 

 (XVI.)

A still more significant coincidence is that the formula (XI) contains three straight chains of seven carbon atoms and all are terminally attached to nitrogen. These chains serve as the basis for the numbering given below and allow us to regard strychnine as the reduction and condensation product of a cyanogenetic glucoside which would, of course, contain the C_6–C–N group.



The chief modifications of the formula (XI) that could be made appear to be the following, and various combinations of these are obviously possible. We have selected a definite formula for purposes of illustration only and the alternatives are not excluded.

(1) Some of the rings may be bridged-rings. For instance, C-10 may be attached, not to C-11, but to C-13 or C-14, preserving in the latter case the three chains of seven carbon atoms. This view is a serious alternative, for it has the advantage that the hydro-indole nucleus is blocked and the formation of carbazole involves less stripping off of external groups.

C-20 also might be attached to some other carbon atom, for example, C-10. This spoils the three chains of seven carbon atoms but gives a curbine formula not containing the group –CO·CH(OH)–.

(2) The carbon atoms 8, 9, and 10 may take the *iso*-form $-CH_2\cdot CHMe-$. In certain cases this is also possible for 15, 16, 17.

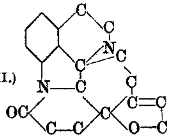
(3) The ring oxygen may be attached to C-11, giving different but analogous formulæ for the Leuchs series of degradation products. This alternative requires that C-8 should be the point of oxidation, $-N-CH_2- \longrightarrow -N-CO-$. The attachment of the ring oxygen to C-17 we consider to be improbable in view of the alkaline decomposition of brucinolic acid which gives, as the primary product, brucinolone-a containing the group $-N\cdot CO\cdot CH_2\cdot CH{=}\overset{|}{C}-$, and this is further transformed by alkali into brucinolone-b characterised by the group $-N\cdot CO\cdot CH{=}CH-\overset{|}{C}H-$ (Leuchs and co-workers, *loc. cit.*). We are of the opinion that a group $-N\cdot CO\cdot CH_2\cdot \underset{O\cdot CH_2\cdot CO_2H}{CH}-\overset{|}{C}H-$ would give, in the first instance, the αβ-unsaturated substance on fission in alkaline solution.

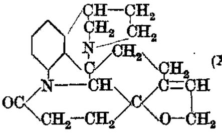
The view which we have put forward in relation to strychnidone (XIV) is also untenable if the ring oxygen is attached to C-17.

(4) The work of Lions, Perkin, and Robinson (Part III, J., 1925, **127**, 1158) showed that the methoxyls in brucine are situated in the ortho-position to one another and that there can be no free position para to either of the methoxyls. Thus the methoxyls may occupy the positions 4 and 5 as in (X) or positions 3 and 4.

(5) Going back to the alternative (VII), which was temporarily set aside in view of the less bizarre character of the formulæ based on (VI), the inclusion of a carbazole skeleton and the groups necessary to express the Leuchs degradations gives (XVII) or a very similar skeleton. Two carbon atoms must be added; one of them is required to make b-N tertiary, and the other to provide the carboxyl group of dinitrostrycholcarboxylic acid. This leads to the strychnine formula (XVIII) or bridged-ring alternatives.

The decision between structures based on (VI) and those based on (VII) can best be made by a synthesis of dinitrostrychol, which we are attempting at the present time.

(XVII.) 

 (XVIII.)

Concurrently with the investigations referred to above, we are continuing our study of the reduction products of strychnine and brucine and have been for some time engaged in the careful examination of the crystalline substances formed when the methosulphates

of strychnine and strychnidine are submitted to the action of sodium amalgam. One of the rings can be readily opened in this way and we wish to reserve for a short time the investigation of this interesting decomposition.

THE UNIVERSITIES OF OXFORD AND MANCHESTER, AND
UNIVERSITY COLLEGE, LONDON. [*Received, November 8th*, 1928.]

NOTES.

The Acetylation of Diethylene Oxide. By MORNA MACLEOD.

EXPERIMENTS carried out by Knoevenagel (*Annalen*, 1913, **402**, 133) on the interaction of acetic anhydride with various ethers in the presence of anhydrous ferric chloride suggested a method by which the presence of two oxide rings in ngaione (McDowall, J., 1925, **127**, 2200) might be confirmed and investigated. Some tests were therefore made with compounds of known constitution.

Knoevenagel's results for cineole were verified, and the reaction was then applied to diethylene oxide. Besides some unchanged diethylene oxide, small quantities of glycol diacetate and ββ'-*di-acetoxyethyl ether* were obtained.

$$2\begin{matrix}CH_2\cdot OAc\\ |\\ CH_2\cdot OAc\end{matrix} \xleftarrow{2Ac_2O} O{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}O \xrightarrow{Ac_2O} O{<}\begin{matrix}CH_2\cdot CH_2\cdot OAc\\ CH_2\cdot CH_2\cdot OAc\end{matrix}$$

The latter compound was a moderately viscous, sweet-smelling oil, b. p. 110—135°/16 mm., $d_{20°}^{20°}$ 1·123, $n_D^{20°}$ 1·4348, whence $[R_L]_D$ = 44·12 (Found: C, 50·9; H, 7·3; sap. value, 582. $C_8H_{14}O_5$ requires C, 50·5; H, 7·4%; $[R_L]_D$, 43·98; sap. value, 589).—THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY, UNIVERSITY COLLEGE, LONDON. [*Received, October 8th*, 1928.]

The Nitration of o-*Bromoacetanilide.* By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON.

THE nitration of *o*-bromoacetanilide proceeds readily according to the method of Franzen and Engel (*J. pr. Chem.*, 1921, **102**, 188), but their description of the separation of the isomeric mononitration products is a little confused. They agitated the finely divided crude nitration product with ice-cold "Witt–Utermann solution" (75 g. of potassium hydroxide, 475 c.c. of water, 100 c.c. of ethyl alcohol). 2-Bromo-6-nitroacetanilide was said to dissolve, and 2-bromo-4-nitroacetanilide was left undissolved. It was further stated that when the solution of the 6-nitro-compound was kept at room

temperature for 24 hours, hydrolysis took place and 2-bromo-nitroaniline was precipitated.

It has now been found that the crude nitration product is alm completely soluble in the " Witt–Utermann solution," only 2 remaining undissolved. The filtrate becomes turbid and after 15 20 minutes a yellow solid begins to separate, precipitation bei complete after 24 hours. This crude product had m. p. 94—9 and after crystallisation from benzene–ligroin (b. p. 60—80°) h m. p. 104°, the melting point of 2-bromo-4-nitroaniline. T nature of this compound was further verified by bromination acetic acid solution, the dibromonitroaniline, m. p. 206°, obtain being identical with 2 : 6-dibromo-4-nitroaniline prepared by t bromination of *p*-nitroaniline.

The filtrate remaining after the separation of the 2-bromo nitroaniline from the " Witt–Utermann solution," on treatment wi glacial acetic acid gave a precipitate of a substance which crystallis from methyl alcohol in long needles, m. p. 193°, the melting poi of 2-bromo-6-nitroacetanilide. On boiling a solution of this su stance (5 g.) in alcohol (24 c.c.) and hydrochloric acid (12 c.c.) 3 hours, hydrolysis took place, the 2-bromo-6-nitroaniline havi m. p. 74—75° after recrystallisation from ligroin (b. p. 40—6 (compare Meldola and Streatfeild, J., 1898, **73**, 686, who give m. 73—74°).

Chattaway, Orton, and Evans (*Ber.*, 1900, **33**, 3061) obtain 2-bromo-4-nitroacetanilide (m. p. 129°) by the action of ace chloride in acetic acid on 2-bromo-4-nitroaniline. Körner (*A R. Accad. Lincei*, 1914, **22**, i, 825), using acetic anhydride, obtair a monoacetyl derivative, m. p. 114°, and a diacetyl derivati m. p. 132°. On repeating the work of the former authors, it w found that the monoacetyl derivative is indeed formed and l m. p. 132—133° (Found : N, 11·1. Calc. : N, 10·8%. T *diacetyl derivative requires* N, 9·3%). This *monoacetyl* derivati contrary to the statement of Franzen and Engel, is readily solu in " Witt–Utermann solution."

All the *o*-bromoacetanilide used in the work was prepared fr *o*-bromoaniline, b. p. 110·5°/19 mm. From 204 g. of pure *o*-bron acetanilide, 66 g. of pure 2-bromo-4-nitroaniline and 80 g. of p 2-bromo-6-nitroacetanilide were obtained.—Guy's Hospital Me cal School (University of London), S.E. 1. [*Receiv September 17th*, 1928.]

CCCCV.—*The Alkaloids of Some Indian Aconites. Part II. Pseudaconitine.*

By Thomas Marvel Sharp.

Most of the species of *Aconitum* which have been examined chemically have been found to contain alkaloids, each species in general yielding a different alkaloid; pseudaconitine has, however, been obtained from two species, *Aconitum deinorrhizum* and *A. Balfourii*. The alkaloids may be subdivided into (*a*) poisonous alkaloids of the aconitine type and (*b*) relatively non-toxic alkaloids of the atisine type. With the exception of lycaconitine (Schulze and Bierling, *Arch. Pharm.*, 1913, **251**, 8) and lappaconitine (Schulze and Ulfert, *ibid.*, 1922, **260**, 230; Weidemann, *Arch. Exp. Path. Pharm.*, 1922, **95**, 166) the alkaloids of the former type (*a*) are similar in that they are all diacyl esters of other bases which are generically called "aconines," *e.g.*, aconine, japaconine, pseudaconine, bikhaconine; in each of these cases one of the groups is acetyl. Aconitine, the best known of the alkaloids, is derived from a European species, *A. Napellus*, and is acetylbenzoylaconine. Two interesting reactions of this alkaloid have been described by Dunstan and collaborators (Dunstan, Tickle, and Jackson, P., 1898, **14**, 159; Dunstan and Carr, J., 1894, **65**, 176). When aconitine is heated in a sealed tube with methyl alcohol, the acetyl group is replaced by a methyl group with the formation of methylbenzoylaconine. The second reaction is also concerned with the acetyl group: when the dry base is heated slightly above its melting point, one molecule of acetic acid is split off and a new base, pyraconitine, is formed. The latter reaction has been shown to be general for those aconitine alkaloids which contain an acetyl group (Dunstan and Carr, *loc. cit.*; J., 1897, **71**, 358; Dunstan and Read, J., 1900, **77**, 60; Dunstan and Andrews, J., 1905, **87**, 1631, 1648; Majima and Suginomé, *Ber.*, 1924, **57**, 1466; Majima and Morio, *ibid.*, p. 1472) and has been studied in some detail in the cases of aconitine and japaconitine by Schulze and Liebner (*Arch. Pharm.*, 1913, **251**, 453; 1916, **254**, 567).

Formula (I) summarises what is at present known regarding the constitution of pseudaconitine.

$$\text{(I.)}\quad C_{19}H_{21}\begin{cases}(O{\cdot}CH_3)_4(CH{\cdot}OH)(N{\cdot}CH_3)(OH)(O{\cdot}CO{\cdot}CH_3)\\ O{\cdot}CO{\cdot}C_6H_3(O{\cdot}CH_3)_2\end{cases}$$

It was thought that a careful study of the two reactions recorded by Dunstan and collaborators might throw some light on the ··tive positions of the groups present in pseudaconitine, and that

pyropseudaconitine might contain some weakened link, which would be a useful point of attack by oxidation or other degradation process, pseudaconitine having been shown in the previous paper (Henry and Sharp, this vol., p. 1105) to be very resistant to oxidation.

It is now found that when pseudaconitine is heated in a sealed tube with methyl alcohol, the acetyl group is replaced by methyl, and that the same reaction takes place—but more slowly—when the base is boiled under reflux with the alcohol. A similar reaction also takes place when tetra-acetylpseudaconine is treated with either methyl or ethyl alcohol, one and only one of the acetyl groups being replaced by the methyl or ethyl group, the latter being introduced at a much slower rate. It is evident, therefore, that there is some group present in a particular relation to this acetyl group which facilitates the replacement. In an attempt to find such a group, a number of acetyl derivatives of comparatively simple constitution have been prepared and treated with methyl alcohol in this manner, but so far without success. The acetyl group or groups in acetylphenol, diacetylpyrocatechol, diacetylresorcinol, diacetylquinol, triacetylpyrogallol, acetylsalicylic acid, acetylpropenylguaiacol, acetyleugenol, acetyl*iso*eugenol, acetyl*cyclo*hexanol, penta-acetyl-*l*-quercitol, penta-acetylmethylinositol, and hexa-acetylmannitol are not replaced in this way.

As stated by Dunstan and Carr (*loc. cit.*), when pseudaconitine is heated above its melting point it loses acetic acid with the formation of pyropseudaconitine, which has now been crystallised. The operation is best carried out in a vacuum, but it is possible that the reaction takes place in more than one way, since a portion of the product could not be induced to crystallise.

The loss of acetic acid can take place in three ways : (*a*) *by the* removal of acetic acid between the acetyl group and a hydroxyl, in which case an ether linkage will be formed; (*b*) by the removal of a hydrogen atom from a neighbouring carbon atom, in which case a double bond will be formed; (*c*) by the removal of a hydrogen atom from a carbon atom in a remote position, with the formation of a bridged linkage. Pseudaconitine was shown in the previous paper (*loc. cit.*) by indirect means to contain two hydroxyl groups; this is now directly proved by the formation of a diacetyl derivative. In case (*a*), therefore, only a monoacetyl derivative of pyropseudaconitine should be formed; in cases (*b*) and (*c*) pyropseudaconitine should yield a diacetyl derivative, and (*b*) would probably be readily reduced by hydrogen in the presence of an active catalyst. If case (*a*) holds, tetra-acetylpseudaconine, which does not contain a free hydroxyl group, should not lose acetic acid on heating, or if

under reduced pressure on a water-bath. On cooling, a white, crystalline solid (1·25 g.) separated; extraction with ether furnished a further 0·1 g. of the same substance, m. p. 187°, which was identified as veratric acid by mixed melting-point determination. The aqueous mother-liquor was made alkaline with sodium carbonate solution and extracted with chloroform. After drying over sodium sulphate, the chloroform yielded on evaporation a light brown varnish (3·2 g.), which was dissolved in ether, filtered from a little amorphous substance, evaporated to dryness under reduced pressure, and redissolved in dry ether; it then suddenly crystallised in needles. After recrystallisation from dry ether, the substance was obtained in aggregates of prismatic, faintly brown needles, m. p. 172°, $[\alpha]_D$ + 227·5° (c = 1·217 in alcohol) (Found on substance dried at 110° in a vacuum: C, 64·4; H, 8·6; OMe, 26·5; NMe, 4·25. $C_{25}H_{39}O_7N$ requires C, 64·5; H, 8·45; 4OMe, 26·7; NMe, 6·2%). *Pyropseudaconine* is very soluble in organic solvents, and in water, forming an alkaline solution; an aqueous solution acidified with sulphuric acid gave only a faint white precipitate with Mayer's reagent, and a slight, brown, sticky precipitate with iodine in potassium iodide; tannic acid, sodium perchlorate, picric acid, and platinic chloride do not produce precipitates. Gold chloride gives a slight yellow cloudiness.

Acetylation. Pyropseudaconitine (3·6 g.) was boiled under reflux for 1½ hours with acetic anhydride (15 c.c.). The solution was evaporated to dryness, and the residue dissolved in alcohol and again evaporated to dryness, the evaporation with alcohol being repeated three times. The product was then again dissolved in hot alcohol; on cooling, the compound separated in colourless prisms, m. p. 228°, $[\alpha]_D^{19.5°}$ + 28·4° (c = 0·537 in chloroform) [Found in substance dried at 120° in a vacuum: C, 63·4, 63·3; H, 7·2, 7·05; OMe, 21·2; NMe, 2·3; acetic acid (see below), 23·4. $C_{39}H_{51}O_{13}N$ requires C, 63·1; H, 6·9; 5OMe, 20·9; NMe, 3·9; $3CH_3{\cdot}CO_2H$, 24·3%]. It is evident, therefore, that the substance is *triacetyldemethylpyropseudaconitine,* formed by the replacement of a methyl by an acetyl group and the acetylation of two hydroxyl groups.

Hydrolysis of Triacetyldemethylpyropseudaconitine.—Dry, finely powdered triacetyldemethylpyropseudaconitine (1·9699 g.) was suspended in 150 c.c. of neutral alcohol, potassium hydroxide (2 c.c. of 50% aqueous solution) added, and the mixture kept at room temperature for 24 hours. The clear solution was then exactly neutralised with sulphuric acid, sufficient water added to dissolve the precipitated potassium sulphate, and the alcohol removed in a current of steam generated from freshly-boiled distilled water free from carbon dioxide. The solution was acidified with sulphuric

triacetyldemethylpyropseudaconitine. The residue from the steam-distillation was cooled, made alkaline with sodium carbonate, and extracted with chloroform. The chloroform on evaporation yielded a pale brown varnish, which, after solution in ether, was obtained in stout, prismatic needles, m. p. 173—174°, $[\alpha]_D + 230{\cdot}1°$ ($c = 1{\cdot}12$ in alcohol). A solution of the base acidified with sulphuric acid gave a faint white precipitate with Mayer's reagent, a slight, brown, pasty precipitate with iodine in potassium iodide solution, and no precipitate with picric acid, tannic acid, sodium perchlorate, or platinic chloride. Auric chloride caused a slight yellow cloudiness. A mixed melting-point determination with pyropseudaconine obtained by the hydrolysis of pyropseudaconitine showed no depression. The products obtained by the hydrolysis of either pyropseudaconitine or triacetylpyropseudaconine are thus identical.

In order to test whether a double bond had been introduced into the molecule in the splitting off of acetic acid, triacetylpyropseudaconine (0·5 g.) was dissolved in alcohol (20 c.c.), and shaken with hydrogen under 3 atmospheres pressure with the addition of an active palladium–barium sulphate catalyst (0·1 g.) for 2 hours; no hydrogen was absorbed. The catalyst was filtered off, the filtrate evaporated to dryness, and the residue dissolved in 50% alcohol; unchanged triacetylpyropseudaconine then crystallised in characteristic six-sided plates, m. p. 155—158° (yield, quantitative).

Action of Heat on Pseudaconine.—It was thought that pseudaconine, on being strongly heated, might lose water with the formation of pyropseudaconine. A quantity of the base crystallised from acetone was therefore placed in a weighing bottle in the apparatus described above and heated at 120—130°. The compound frothed with loss of 1 mol. of acetone, which was collected in water and identified by conversion into iodoform (Found: loss at 120—130°, 10·4. $C_{25}H_{41}O_8N,C_3H_6O$ requires loss, 10·7%). The temperature was raised to 150° and then by successive rises of 10° to 210°, at which temperature the first loss in weight was observed. At this temperature also a ring of varnish collected on the cooler part of the reaction tube and the substance began to darken; it was evidently beginning to distil (with slight decomposition), since pseudaconine was recovered from the heated substance in a yield of 90%.

Veratroylmethylpseudaconine.—Pseudaconitine (5 g.) was heated in a sealed tube at 130° for 6 hours with 35 c.c. of methyl alcohol. The alcohol was removed and the residue was dissolved in 1% hydrochloric acid, made alkaline with sodium carbonate, and extracted with ether. The ether soon began to deposit crystals; from 's, however, found convenient to distil the ether and convert

e residue (5 g., not completely dried) into the **hydrobromide**, ıich separated from water in colourless crystals containing $1H_2O$, . p. 237—238° (with efferv.), $[\alpha]_D + 2\cdot15°$ ($c = 2\cdot09$ in water) Found: loss at 120° in a vacuum, 2·6. $C_{35}H_{51}O_{11}N,HBr,H_2O$ equires loss of $1H_2O$, 2·4%. Found on anhydrous substance: C, 6·3, 56·5: H, 7·5, 6·8; N, 1·9; OMe, 28·75; NMe, 2·55; Br, 11·1. $C_{35}H_{51}O_{11}N,HBr$ requires C, 56·6; H, 7·1; N, 1·9; 7OMe, 29·3; NMe, 3·9; Br, 10·8%). The *base*, prepared from the purified ıydrobromide, crystallised from 50% alcohol in colourless prisms, m. p. 206—207°, $[\alpha]_D + 29\cdot8°$ ($c = 1\cdot12$ in alcohol) (Found on substance dried at 120° in a vacuum: C, 63·7; H, 7·9; OMe, 33·0; NMe, 2·8. $C_{35}H_{51}O_{11}N$ requires C, 63·5; H, 7·8; 7OMe, 32·9; NMe, 4·4%). The *hydrochloride* crystallised from alcohol–ether in hard, hemispherical aggregates of colourless needles, m. p. 249—250° (decomp.), $[\alpha]_D - 3\cdot41°$ ($c = 5\cdot43$ in water), $+ 0\cdot38°$ ($c = 2\cdot62$ in alcohol) (Found: Cl, 5·1. $C_{35}H_{51}O_{11}N,HCl$ requires Cl, 5·1%).

Acetylation. (a) *Acetic anhydride.* Veratroylmethylpseudaconine (2 g.) was boiled under reflux for an hour with acetic anhydride (10 c.c.). Excess of the reagent was distilled off, the residue dissolved in 1% hydrochloric acid, and sodium perchlorate solution added in excess. The white precipitate was washed well with water and dried in a desiccator (2·2 g.). After crystallisation from absolute alcohol, the *perchlorate* was obtained in stout, colourless needles, m. p. 240—242° (Found on substance dried at 110° in a vacuum: OMe, 26·9; NMe, 2·2. $C_{37}H_{53}O_{12}N,HClO_4$ requires 7OMe, 27·0; NMe, 3·6%). Acetyl groups were estimated in the manner already described (p. 3098), but owing to the sparing solubility of the salt more alcohol was required (300 c.c. for 0·7 g.) and the mixture was kept for 40 hours (Found: acetic acid, 8·5. $C_{37}H_{53}O_{12}N,HClO_4$ requires for 1 mol. of acetic acid, 7·5%). The substance is therefore a *monoacetylveratroylmethylpseudaconine perchlorate*. The mother-liquor from the steam distillation of the acetic acid was extracted with ether, which removed veratric acid (0·17 g.), made alkaline with ammonia, and extracted with chloroform. The chloroform furnished on evaporation a light brown varnish (0·5 g.), which wa not obtained crystalline but must have been methylpseudaconine It was very soluble in water and in most organic solvents and di not give any crystalline salt.

The formation of a monoacetyl derivative was unexpected i view of the fact that pseudaconitine contains two hydroxyl group which should have remained intact in the replacement of an acet by a methyl group. A diacetyl derivative was, however, obtain by acetylation with acetyl chloride.

(b) *Acetyl chloride.* Veratroylmethylpseudaconine (2·5 g.) w

boiled under reflux for an hour with acetyl chloride (12 c.c.). Excess of the reagent was evaporated, and the residue dissolved in water and made alkaline with ammonia: the white precipitate which formed was washed well with water and dried. After crystallisation from absolute alcohol *diacetylveratroylmethylpseudaconine* was obtained in colourless needles or compact crystals (2·2 g.). Either form melts at 160°, resolidifies after a time, and then remelts at 196°; $[\alpha]_D + 18·43°$ in chloroform ($c = 1·248$) (Found on substance dried at 120° in a vacuum : OMe, 28·65; NMe, 2·1; acetic acid, 16·5. $C_{39}H_{55}O_{13}N$ requires 7OMe, 29·1; NMe, 3·9; $2CH_3·CO_2H$, 16·1%). Methylpseudaconine and veratric acid were recovered from the mother-liquor from the determination of acetyl groups in the manner described under monoacetylveratroylmethylpseudaconine (see above).

Triacetylmethylpseudaconine.—Tetra-acetylpseudaconine (2 g.) was heated in a sealed tube at 130° for 5 hours with methyl alcohol (25 c.c.). The product, which crystallised on cooling, separated from alcohol in colourless needles, m. p. 280—282°. The melting point varies with the rate of heating. Yield, 1·65 g., $[\alpha]_D - 18·5°$ ($c = 0·766$ in alcohol) (Found : C, 61·7; H, 7·9; OMe, 24·8; NMe, 3·7. $C_{32}H_{49}O_{11}N$ requires C, 61·6; H, 7·9; 5OMe, 24·9; NMe, 4·7%). Crystalline salts could not be obtained.

Triacetylethylpseudaconine.—In the first preparation of tetra-acetylpseudaconine (this vol., p. 1112) the compound was crystallised from ethyl alcohol and during the crystallisation to constant melting point and rotation small crops with a higher melting point and higher rotation were obtained. After a long and tedious fractionation involving more than 40 fractional crystallisations, a quantity of material was obtained whose melting point (171°) and rotation ($[\alpha]_D - 25·17°$ in alcohol, $c = 1·023$) were unaltered on subsequent recrystallisations; this on analysis proved to be *triacetylethylpseudaconine*. An attempt was made to prepare this compound in a simpler manner by heating tetra-acetylpseudaconine (2 g.) in a sealed tube at 120° for 47 hours with 25 c.c. of absolute alcohol. The product crystallised on cooling. After recrystallising twice from ethyl alcohol, 0·5 g. of colourless needles, m. p. 171°, $[\alpha]_D - 26°$ in alcohol ($c = 0·98$), were obtained, identical with the compound obtained in the fractional crystallisation of tetra-acetylpseudaconine. Subsequent crops of crystals consisted of mixtures of the two compounds (Found : C, 62·1; H, 8·2; N, 2·2; OMe, 24·0; NMe, 3·1. $C_{33}H_{51}O_{11}N$ requires C, 62·1; H, 8·1; N, 2·2; 4OMe + OEt calc. as 5OMe, 24·3; NMe, 4·55%). Crystalline salts could not be obtained.

Hydrolysis. Triacetylethylpseudaconine (3·0640 g.) was dissolved

chloric acid and once with water. These two extracts were added to the first aqueous layer and the whole was extracted with ether. This extract was added to the main ethereal extract; on evaporation a mixture of benzoic acid and benzoyl chloride was obtained. The aqueous extract was warmed and agitated to remove dissolved ether, cooled, and treated with excess of sodium perchlorate solution. The precipitated perchlorate was washed well with water, dried in a desiccator, and crystallised from absolute alcohol. It formed confused colourless prisms, m. p. 236° (efferv.). Yield, 0·75 g. There remained an uncrystallisable residue (Found: OMe, 21·1, 21·0; NMe, 2·05, 1·8. $C_{43}H_{55}O_{13}N,HClO_4$ requires 6OMe, 20·8; NMe, 3·25%). The acetyl and benzoyl groups were estimated together by cold hydrolysis with alcoholic potassium hydroxide followed by steam distillation and titration of the volatile acids [0·7434 g. of substance yielded volatile acid equivalent to 3·1 c.c. of 0·5218*N*-sodium hydroxide: volatile acid, 13·05 (calc. as acetic). $C_{43}H_{55}O_{13}N,HClO_4$ requires volatile acid (1 acetic + 1 benzoic acid calc. as acetic), 13·4%]. The acids were separated and identified by evaporation of the neutralised steam distillate to a small volume, acidification, and extraction with much light petroleum (b. p. 90—120°), which removed the benzoic acid and left the acetic acid in solution. The petroleum extract was shaken with sodium hydroxide solution, and the alkaline liquid acidified and extracted with ether, which furnished 0·1 g. of benzoic acid on evaporation, identified by its melting point (after sublimation), 121—122°, its smell, and the smell of ethyl benzoate obtained on warming it with alcohol and sulphuric acid. The acid mother-liquor from the petroleum extract was neutralised with sodium hydroxide, evaporated to dryness, and extracted with alcohol to dissolve the sodium acetate. The alcohol was evaporated, the sodium salt dissolved in water, and the silver salt precipitated by silver nitrate (Found: Ag, 63·3. Calc. for $CH_3·CO_2Ag$: Ag, 64·7%). The residue from the steam distillate was extracted with ether (which gave veratric acid), made alkaline with sodium hydroxide, and extracted with chloroform. The latter, on evaporation, left a varnish, from which pseudaconine was obtained on crystallisation from acetone, m. p. 92—94°, $[\alpha]_D$ + 36·2°. The benzoylation product is therefore *monobenzoylpseudaconitine perchlorate*. The base was prepared from the purified perchlorate by treatment in alcoholic solution with an alcoholic solution of potassium acetate, but it was not obtained crystalline, nor could any other crystalline salt be obtained.

Acetylation of Pseudaconitine.—Pseudaconitine (2 g.) was boiled under reflux for an hour with 8 c.c. of acetyl chloride, the excess of the reagent distilled off, and the residue dissolved in water,

A similar result was obtained with the base in alcohol, Adams's platinum oxide catalyst and a trace of ferric chloride being used ("Organic Syntheses," vol. 8, p. 92).

The author desires to thank Dr. T. A. Henry for his kind advice and criticism, and Mr. H. C. Clarke for his assistance in the preparation and analysis of the products described.

WELLCOME CHEMICAL RESEARCH LABORATORIES,
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CCCCVI.—*The Action of Bromine on Strontium Oxide and its Hydrates.*

By HORACE BARRATT DUNNICLIFF, HARNAM DAS SURI, and KISHEN LAL MALHOTRA.

THE action of halogens on slaked lime was studied by Wilks (J., 1912, **101**, 366), and we now describe the action of bromine both as vapour and as a solution in carbon tetrachloride on strontium oxide and its hydrates.

The Action of Bromine on Anhydrous Strontium Oxide.—Merck's pure strontium oxide was used. Pure carbon tetrachloride (Kahlbaum) was distilled over calcium chloride; and bromine was purified by a modification of Brauner's method (*J. Amer. Chem. Soc.*, 1920, **42**, 921). After exposure to bromine vapour for some days, strontium oxide adsorbed about 1% of its weight of bromine, giving a pale dirty-brown product containing a few scarlet specks. The same proportion of bromine is adsorbed under identical conditions by dry, powdered silica. Strontium oxide shaken with a 2% solution of bromine in carbon tetrachloride for 48 hours took up 1·5% of its weight of bromine, as determined by loss of bromine from the solution. In both cases the solid lost the adsorbed bromine on exposure to the air, so chemical action had not taken place.

The Action of Bromine on Strontium Hydroxide Monohydrate.—Kahlbaum's strontium hydroxide octahydrate was recrystallised in a carbon dioxide-free atmosphere (Found: SrO, 39·15. Calc.: SrO, 39·06%). The powdered octahydrate was extracted with alcohol (b. p. 78·2°/742 mm.) in a Soxhlet apparatus under 150—170 mm. pressure for 10 hours: this is a new method for the preparation of strontium hydroxide monohydrate (Found: SrO, 73·87. Calc.: SrO, 74·21%). When the monohydrate is exposed to excess of bromine vapour, it yields a dark brown substance which resembles -rom-bleaching powder (Wilks, *loc. cit.*), and from which carbon -chloride extracts some bromine. When this substance is kept

Soc., 1909, **31**, 525), and strontium was determined as sulphate (Found : Sr, 32·36 ; Br, extracted by CCl_4, traces ; Br, as bromide, 36·10 ; as hypobromite, 4·54 ; as bromate, nil). The bromide and hypobromite correspond to 61·3% of the strontium present. Thus, when treated either with bromine vapour or with bromine in carbon tetrachloride, strontium hydroxide monohydrate gives appreciable amounts of hypobromite. Reference to the action of bromine on the octahydrate (below) shows that, when greater quantities of water are present, the hypobromite is decomposed almost as quickly as it is formed.

The Action of Bromine on Strontium Hydroxide Octahydrate.—When strontium hydroxide octahydrate was exposed to bromine vapour, a yellow, gelatinous mass containing droplets of water was formed. After standing in a vacuum desiccator for 48 hours, it contained 37·51% of bromine as strontium bromide and 8·89% as bromate ; hypobromite was absent. These results give a calculated value for strontium as bromide and bromate of 25·40%, whereas the proportion of strontium actually found was 25·16%. Hence the reaction is quantitative.

When first exposed to a solution of bromine in carbon tetrachloride, strontium hydroxide octahydrate turns brown. In the dark or in daylight the colour gradually fades, and a flocculent mass containing droplets of water is formed. After several weeks, colourless, needle-shaped crystals are found on the sides of the vessel and extend far above the level of the solid phase. These crystals (roughly dried, m. p. 92°) are strontium bromide contaminated with a little bromate and water; their formation is accelerated by insolation.

In order to determine the time taken for the completion of the reaction, powdered strontium hydroxide octahydrate (1 g.) was shaken in a number of bottles at 20° with 100 c.c. of a solution of 1·594 g. (19·93 mg.-equivs.) of bromine in carbon tetrachloride for various intervals of time, and the loss of bromine from the liquid phase determined volumetrically. The results (Table II) show that, at first, a rapid chemical reaction with 200 mg. (2·50 mg.-equivs.) of bromine takes place. This is followed by a slower reaction, as shown by the increase in the value of x (mg.-equivs. of bromine consumed) with time (t, in hours), and if allowance be made for the 2·50 mg.-equivs. of bromine used in the primary reaction, a unimolecular velocity coefficient (k) is obtained for the first hour of the second reaction; thus, a being the original concentration of bromine (19·93 mg.-equivs. per 100 c.c.), $a_1 = a - 2{\cdot}50 = 17{\cdot}43$, and putting $x_1 = x - 2{\cdot}50$, we have $k = 1/t \cdot \log a_1/(a_1 - x_1)$. By application of the method of calculation given by Dunnicliff and

From this it is concluded that the hypobromite is formed and decomposed almost immediately, but that, up to 2 hours, the rate of formation exceeds the rate of decomposition. At the end of the reaction, hypobromite is negligible or absent.

TABLE III.

Conc. of Br_2 (g. per 100 c.c.).	$SrBr_2,6H_2O$, %	$Sr(BrO_3)_2,H_2O$, %	Water, %, Found.	Water, %, *Calc.	Strontium, %, Found.	Strontium, %, *Calc.	Mol. ratio, bromide : bromate.
Temperature, 15—17°.							
1·5	76·68	20·14	22·92	24·29	24·43	23·73	3·86
2·0	77·56	21·01	24·30	24·60	24·29	24·20	3·76
2·0	80·72	20·03	23·44	25·51	24·49	24·74	4·10
Temperature, 32—33°.							
1·5	76·79	20·74	—	24·35	24·92	23·94	3·76
3·0	79·54	20·48	—	25·18	24·80	24·56	3·95
3·5	80·56	19·42	—	25·43	—	24·65	4·21

* From columns 2 and 3.

The gelatinous residue from each of several experiments was left in a desiccator until its weight was constant and then analysed. The vapour pressures of the crystalline bromide and bromate are low, and the water content of the final product, as found by heating with lead chromate in a current of dry air, is within reasonable agreement with the value (Table III, col. 5) found by calculation from the water of crystallisation of the salts (Table III, cols. 2 and 3). If, as these results indicate, the preliminary formation of equimolecular quantities of hypobromite and bromide is followed by the rapid decomposition of the hypobromite into bromide and bromate, one would expect the final proportion of bromide to bromate to be 5 : 1. Our ratio is uniformly lower and suggests that, in the presence of sufficient water, the excess of bromine oxidises some of the hypobromite to bromate direct (compare Dietzel and Schlemmer, *Z. anorg. Chem.*, 1925, **145**, 381). The following results, obtained by treating equal quantities of strontium hydroxide octahydrate with a 3% solution of bromine in the dark and in sunlight for 8 hours, show that the formation of bromate is favoured by insolation, and the values in the last two columns show that the reaction is quantitative :

	Br as bromide, %.	Br as bromate, %.	Strontium, %, Found.	Strontium, %, Calc.
In sunlight	34·88	9·86	24·69	24·39
In the dark......	37·78	7·04	24·82	24·54

The Action of Iodine on Strontium Oxide and its Hydrates.—Rama Krishna Bahl has carried out a similar series of experiments with iodine. There was no action with strontium oxide. With the monohydrated hydroxide, the interaction was small and the

The organic acids (except oxalic acid) and their salts are simple examples of solutes with two different groups, and such substances might be expected to show an increased solubility in aqueous alcohol. The values in Table I are taken from Seidell's results

TABLE I.

Solubilities of various organic salts and acids in aqueous ethyl alcohol at 25°.

(G. per 100 g. of solvent.)

	EtOH, % by weight.							
	0%.	10%.		50%.		90%.		100%.
Solute.		Found.	Calc.	Found.	Calc.	Found.	Calc.	
Benzoic acid ...	0·37	0·60	6·18	20·5	29·4	56·3	42·6	58·5
Salicylic acid ...	0·25	0·38	5·19	13·8	25·0	45·7	44·7	49·7
Camphoric acid	0·76	1·62	10·73	45·0	50·6	105·4	90·4	100·5
Stearic acid	0·03	0·04	0·93	0·18	4·54	3·41	8·13	9·05
Tartaric acid ...	137·5	127·3	126·5	88·6	82·5	40·8	38·6	27·6
Na benzoate ...	56·3	54·5	50·7	34·5	28·5	2·88	6·17	0·605
,, salicylate ...	115·5	109	104·3	73·1	59·7	17·6	15·12	3·97
NH_4 benzoate ...	22·9	21·9	20·7	20·4	12·3	4·37	3·77	1·65
,, salicylate ...	103	101·5	93·0	87·7	65·7	46·2	36·2	28·8

(*U.S. Hyg. Labor. Bull. No.* 67) and from his tables, and the calculated values are based on the "mixture" rule. The results are in agreement with the view put forward, the double solvent attraction being that of the alcohol on the hydrocarbon radical and of water on the carboxyl group. It may also be noted that, if the solute is fairly soluble in both constituents, then abnormally high solubility occurs with all proportions of the mixed solvent, whereas if the solute is only slightly soluble in one constituent, then the maximum increase occurs with a mixture rich in the other constituent. Stearic acid shows no exaltation in solubility, but it is almost a hydrocarbon and has a very slight solubility in water, so an exaltation would only be expected in almost absolute alcohol.

In the present paper the work has mainly been confined to an examination of the solubility of acetanilide in a number of binary solvent mixtures. The results (Table II) are in accordance with the views put forward. The solubility in water is probably due to the carbonyl and imino-groups; alcohol will probably act, in addition, on the hydrocarbon portion of the molecule, resulting in an increased solubility for certain compositions of the mixed solvent. The effect should be greater with the higher alcohols, as they have greater solvent power for hydrocarbons. Thus the effect is absent with water–methyl alcohol, and is greater with propyl alcohol than with ethyl alcohol. Again, in alcohol–benzene mixtures, the benzene probably acts only on the phenyl group,

Table II.

Solubilities of acetanilide in mixed solvents at 20°.

(G. per 100 g. of solvent.)

(a) *Aqueous alcohols.*

H_2O + MeOH.

% MeOH (by wt.).	Solubility. Found.	Calc.
100	46·0, 46·0	—
96·2	43·6, 43·7	44·3
93·5	42·0, 42·2	43·0
86·6	37·5, 37·5	39·9
71·7	23·1, 23·2	33·1
49·8	7·2, 7·3	23·1
25·4	1·5, 2·0	12·1
0·0	0·52, 0·52	—

H_2O + EtOH.

% EtOH (by wt.).	Solubility. Found.	Calc.
100	28·8, 28·8	—
95·2	31·3, 31·3	27·5
90·4	32·4, 32·3	26·0
84·2	33·1, 33·1	24·3
74·8	28·8, 29·2	21·6
52·5	13·8, 13·6	15·3
26·3	2·1, 2·2	7·9
0·0	0·52, 0·52	—

H_2O + PrOH.

% PrOH (by wt.).	Solubility. Found.	Calc.
100	22·4, 22·8	—
95·3	28·3, 28·5	21·5
90·0	35·4, 35·4	20·3
85·0	34·0, 33·5	19·3
54·2	18·6, 18·7	12·5
34·5	9·3, 9·3	8·1
16·3	1·8, 1·8	4·1
0·0	0·52, 0·52	—

(b) *Benzene–alcohol mixtures.*

C_6H_6 + MeOH.

% C_6H_6 (by wt.).	Solubility. Found.	Calc.
100	1·05, 1·08	—
81·5	35·4, 34·8	9·4
62·8	49·3, 50·5	17·9
42·5	54·6, 54·5	27·0
21·8	52·9, 52·7	36·3
0·0	46·2	—

C_6H_6 + EtOH.

% C_6H_6 (by wt.).	Solubility. Found.	Calc.
100	1·08, 1·08	—
83·8	21·1, 21·1	5·6
63·8	31·5, 32·0	11·1
41·7	35·7, 35·8	17·2
20·0	33·3, 33·4	23·3
0·0	28·8	—

C_6H_6 + PrOH.

% C_6H_6 (by wt.).	Solubility. Found.	Calc.
100	1·05, 1·08	—
83·0	17·5, 17·5	4·7
58·0	28·3, 28·1	10·[illegible]
42·0	29·7, 29·5	13·[illegible]
18·8	27·7, 27·5	18·[illegible]
0·0	22·6	—

(c) *Mixed alcohols.*

MeOH + EtOH.

% MeOH (by wt.).	Solubility. Found.	Calc.
100	46·2, 46·2	—
83	42·5, 42·5	43·3
71·4	40·6, 40·6	41·2
50·3	37·2, 37·3	37·7
33·7	34·2, 34·3	34·7
17·7	31·4, 31·5	31·9
0·0	28·8, 28·8	—

EtOH + PrOH.

% EtOH (by wt.).	Solubility. Found.	Calc.
100	28·8, 28·8	—
90·0	27·9, 27·9	28·1
79·4	27·7, 27·5	27·3
59·1	26·5, 26·3	25·9
40·7	25·5, 25·4	24·6
19·9	23·9, 23·9	23·2
0·0	21·8, 21·8	—

Pr^αOH + Pr^βOH

% Pr^αOH (by wt.).	Solubility. Found.	C[illegible]
100	21·8, 21·8	[illegible]
83·3	22·9, 23·0	[illegible]
71·2	23·3, 23·6	[illegible]
46·2	24·9, 25·0	[illegible]
24·7	25·6, 25·4	[illegible]
0·0	25·9, 25·9	[illegible]

5 : 7 : 4′-*trimethoxy-2-styryl*iso*flavone*. We wish to direct particular attention to this modification of the usual procedure, since we have found in other cases that it is remarkably effective.

Several attempts to prepare derivatives of genisteincarboxylic acid by oxidation of the acetyl derivative of (I) were unsuccessful, but the methyl ether could be oxidised by means of potassium permanganate in aqueous pyridine solution with formation of benzoic acid and 5 : 7 : 4′-*trimethoxy*iso*flavone-2-carboxylic acid* (II). This acid decomposes smoothly, when heated above its melting point, yielding 5 : 7 : 4′-*trimethoxy*iso*flavone* (III) or genistein trimethyl ether. The latter has not yet been obtained from genistein, but on demethylation it furnished 5 : 7 : 4′-trihydroxy*iso*flavone (IV), identical in all respects with genistein from *Genista tinctoria*, Linn. (Perkin and Newbury, J., 1899, **75**, 830), a specimen of which was very kindly sent to us by Professor A. G. Perkin.

EXPERIMENTAL.

5-*Hydroxy*-7 : 4′-*dimethoxy-2-styryl*iso*flavone* (I).—Methyl sulphate and aqueous potassium hydroxide (40%) were added in small portions alternately and with shaking to a solution of 5 : 7-dihydroxy-4′-methoxy-2-styryl*iso*flavone (Part II, *loc. cit.*) (7·5 g.) in methyl alcohol (100 c.c. of 50%) and potassium hydroxide (10 g.). The deep orange-yellow colour of the solution faded. The precipitated methylated product, after being washed successively with dilute aqueous potassium hydroxide, water, and alcohol, crystallised from much alcohol in tiny, bright yellow needles, m. p. 245—246° (Found : C, 74·8; H, 5·2. $C_{25}H_{20}O_5$ requires C, 75·0; H, 5·0%). The phenolic function is feebly exercised, since, although the alcoholic solution becomes greenish-brown on the addition of ferric chloride, the substance is insoluble in dilute caustic alkali solution. The solution in sulphuric acid is intensely yellow and exhibits a weak green fluorescence.

The *acetyl* derivative was prepared in the usual manner by means of acetic anhydride. It crystallised from alcohol in thin, yellow prisms, m. p. 203—204° (Found : C, 73·1; H, 5·2. $C_{27}H_{22}O_6$ requires C, 73·3; H, 5·0%). Hydrolysis regenerated 5-hydroxy-7 : 4′-dimethoxy-2-styryl*iso*flavone, m. p. 245—246°. Attempts to oxidise this derivative to *O*-dimethylgenisteincarboxylic acid by means of potassium permanganate in acetone at − 10° to − 15° and in pyridine were fruitless.

5 : 7 : 4′-*Trimethoxy-2-styryl*iso*flavone* (Methyl ether of I).—Methyl sulphate (100 c.c.) and aqueous sodium hydroxide (100 c.c. of 20%) were added to a solution of 5-hydroxy-7 : 4′-dimethoxy-2-styryl*iso*flavone (10 g.) in acetone (400 c.c.). The mixture was

not cooled and the acetone layer, at first orange, became lemon-yellow; thereupon aqueous sodium hydroxide (50 c.c. of 20%) and methyl sulphate (50 c.c.) were added. Subsequently the liquid was kept strongly alkaline by the further gradual addition of 20% sodium hydroxide (100 c.c.). The product, obtained in theoretical yield, was precipitated by water (500 c.c.) and collected. It gave no coloration with ferric chloride in alcoholic solution and crystallised from alcohol in pale yellow, iridescent needles, m. p. 193° (Found : C, 75·3; H, 5·3. $C_{26}H_{22}O_5$ requires C, 75·4; H, 5·3%). The crystals are plank-shaped with obliquely cut ends and give an intensely yellow solution in sulphuric acid.

5 : 7 : 4′-*Trimethoxy-2-styryl-6(?)-methylisoflavone*, prepared in a like manner from 5-hydroxy-7 : 4′-dimethoxy-2-styrylmethyl*iso*-flavone (Part II, *loc. cit.*), crystallised from alcohol in pale yellow needles, m. p. 211° with some previous shrinking (Found : C, 75·9; H, 5·7. $C_{27}H_{24}O_5$ requires C, 75·7; H, 5·6%). A mixture of this nuclear methylated compound with its lower homologue (m. p. 193°) melted at 175—180°.

5 : 7 : 4′-*Trimethoxyisoflavone-2-carboxylic Acid* (II).—A solution of potassium permanganate (15 g.) in water (500 c.c.) at about 30° was rather quickly added to one of 5 : 7 : 4′-trimethoxy-2-styryl*iso*-flavone (9 g.) in pure pyridine (500 c.c.) at about 35°. The oxidation was accompanied by a considerable rise of temperature. When the permanganate was reduced, the solution was filtered and distilled under about 100 mm. pressure until the liquid clouded and frothed excessively. The mixture was at once rendered strongly acid and while still warm the precipitated sticky orange mass was taken up in ethyl acetate. The extract was washed with water and then with aqueous sodium carbonate; the latter washings gave an ochreous precipitate on acidification. This was collected and heated with a little acetic acid in order to dissolve the impurities; the colourless, sandy residue (0·78 g.) was practically pure *trimethoxyisoflavone-carboxylic acid*. This derivative crystallises from acetic acid, in which it is very sparingly soluble, in satiny, microscopic, well-formed prisms, m. p. 237° (sharp but with immediate rapid decomposition) (Found : C, 63·8; H, 4·7. $C_{19}H_{16}O_7$ requires C, 64·0; H, 4·5%).

5 : 7 : 4′-*Trimethoxyisoflavone* (III).—The foregoing carboxylic acid was carefully heated above its melting point; the product crystallised several times from methyl alcohol in colourless, glistening, prismatic needles, m. p. 162—163° (Found : C, 69·1; H, 5·4. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·2%). It also separated under some undetermined conditions in rhombic plates, m. p. 162—163°.

5 : 7 : 4′-*Trihydroxyisoflavone* (Genistein, Prunetol, IV).—For the demethylation, the trimethyl ether was recovered from the methyl-

alcoholic mother-liquor, 0·52 g., m. p. 159—161°, being obtained. This was dissolved in a boiling mixture of acetic acid (10 c.c.) and acetic anhydride (5 c.c.), and colourless hydriodic acid (25 c.c., *d* 1·7) gradually introduced. After 20 minutes' boiling, two-thirds of the liquid was removed by distillation and water and sulphurous acid were added. The product was collected and acetylated by boiling for 30 minutes with acetic anhydride and a drop of pyridine. The acetyl derivative was isolated, crystallised once (m. p. 195—198°) from methyl alcohol, and then hydrolysed by boiling dilute aqueous sodium hydroxide and a few drops of alcohol. The recovered phenol crystallised from aqueous alcohol in long, colourless needles, m. p. 290—291° after softening and reddening at about 284°. A mixture with natural genistein and the latter alone exhibited an identical behaviour.

The synthetical specimen showed all the reactions of genistein as described in Part II (*loc. cit.*), and finally the characteristic dimethyl ether, m. p. 140—142°, was prepared and directly compared (mixed m. p.) with a specimen of natural origin (actually from prunetin), but no divergences of properties were noticed.

THE UNIVERSITY, MANCHESTER. [*Received, October 17th,* 1928.]

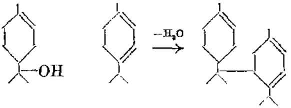
CCCCIX.—*The Oxidation of Dipinene.*

By LINDSAY HEATHCOTE BRIGGS and WALLACE FRANK SHORT.

THE methods which have been employed for the conversion of mono- and di-cyclic terpenes and their derivatives into diterpenes have been reviewed by Kondakov and Saprikin (*Bull. Soc. chim.*, 1925, **37**, 918, 1045. See also Carter, Read, and Smith, *J. Soc. Chem. Ind.*, 1925, **44**, 543T). No definite crystalline addition compounds have been obtained from these synthetic diterpenes, and it is suggested in the communications mentioned above that this is due to the presence of various isomeric diterpenes.

Kondakov and Saprikin suggested that the diterpenes obtained from pinene by the action of various polymerising agents (sulphuric acid, ferric chloride, fuller's earth, etc.) contain two six-membered rings united through a *gem*-dimethyl group, and that *cyclo*propane and *cyclo*butane rings are probably also present. Carter, Read, and Smith, on the other hand, suggested that the diterpenes which they obtained by the action of phosphoric acid on pinene, limonene, and cineole were possibly formed owing to the production and subsequent condensation of terpinene and terpineol. The terpineol

residue might become attached to position 5, 6, 7, or 8 in the terpinene molecule :



No well-characterised oxidation products have hitherto been obtained from any of the diterpenes produced by the polymerisation of mono- and di-cyclic terpenes. By applying the method of "dehydrogenating disruption" with manganese dioxide and sulphuric acid, developed by Ruzicka, to a dipinene produced by the action of hydrogen chloride and ferric chloride upon pinene, we have obtained an oxidation product from which trimellitic, terephthalic, and benzoic acids were isolated. This result supports the suggestion that diterpenes of this type contain two hexagonal nuclei united through a chain of one or two carbon atoms. Further deductions would, however, be unwarranted, because it is now well known (Carius, *Annalen*, 1868, **148**, 50; Ruzicka and Rudolph, *Helv. Chim. Acta*, 1927, **10**, 917) that some of the benzenecarboxylic acids obtained by oxidation with manganese dioxide and sulphuric acid are not produced normally from the carbon framework of the oxidised substance, but contain adventitious carboxyl groups.

EXPERIMENTAL.

Preparation of Dipinene.—Moist hydrogen chloride was passed into a mixture of 300 g. of pinene (b. p. 155—160°; $[\alpha]_{5790}^{18°}$ − 24·4°) with light petroleum (250 c.c.) until 87 g. had been absorbed. After another 300 g. of pinene had been added, anhydrous ferric chloride (30 g.) was introduced in small portions with stirring. This caused the solution to boil, and, after it had cooled, it was washed with sodium hydroxide and water and dried over sodium sulphate. The solvent was then removed and the residue distilled in a vacuum. The diterpene fraction was repeatedly distilled, finally over sodium, through a 10 cm. Vigreux column and 77 g. of a colourless oil were ultimately obtained, b. p. 183—184°/15 mm., $d_{4°}^{20°}$ 0·9260, $n_D^{20°}$ 1·5174, $[R_L]_D$ 88·92 (calc. for a dicyclic diterpene, 88·76).

Oxidation of Dipinene.—A preliminary experiment showed that the physical constants were only very slightly changed when dipinene was boiled with 57% sulphuric acid for 36 hours.

Powdered manganese dioxide (370 g. of 82%) was added in small portions during ½ hour to a mixture of dipinene (22 g.), concentrated sulphuric acid (500 c.c.), and water (600 c.c.). After the mixture

had been refluxed for $2\frac{1}{2}$ days, manganese dioxide (100 g.) and concentrated sulphuric acid (175 c.c.) were added and the boiling was continued until solution of the oil was complete (1 day). The product was diluted with an equal volume of water and filtered while still warm. The residual manganese dioxide was digested at 100° with dilute sodium hydroxide solution, the filtered alkaline liquid added to the acid filtrate, and the whole exhaustively extracted with alcohol-free ether. The dark brown product (approx. 6 g.) obtained was dissolved in dilute ammonia, filtered from a small quantity of gelatinous material, neutralised, and precipitated with silver nitrate. The silver salts, after being dried at 60° in a vacuum for 24 hours, were mixed with dry methyl iodide (7 g.) and absolute ether (10 c.c.), and the mixture, which became warm, was finally heated under reflux (3 hours) to complete the reaction. The product was diluted with ether, filtered, extracted with dilute sodium hydroxide solution, washed with water, and dried. (The alkaline layer contained an insignificant amount of organic material.) The residue obtained by removal of the ether was distilled in a vacuum and the following fractions were collected: (1) b. p. 50—60°/5 mm. (1·1 g.), (2) 70—80°/0·2 mm. (1·1 g.), (3) 80—140°/0·2 mm. (0·6 g.), (4) 140—150°/0·2 mm. (2·4 g.).

Fraction (1) was hydrolysed by alcoholic potassium hydroxide and yielded benzoic acid, m. p. 119—121° (Found for the silver salt: Ag, 47·3. Calc.: Ag, 47·1%) (*p*-nitrobenzyl ester, m. p. 88—89°).

Fraction (2) was recrystallised three times from hot methyl alcohol and then melted at 137—138° (methyl terephthalate melts at 140°). The acid obtained by hydrolysis sublimed without melting and was identified with terephthalic acid by analysis of the silver salt (Found: Ag, 56·5. Calc.: Ag, 56·8%) and by conversion into the *p*-nitrobenzyl ester, m. p. 263·5°.

Fraction (3) was recrystallised from methyl alcohol, but no homogeneous substance could be isolated.

Fraction (4) was only partly saponified by alcoholic potassium hydroxide and was therefore hydrolysed by heating at 150° for 8 hours with concentrated hydrochloric acid (4 parts) (compare Ruzicka, Schinz, and Meyer, *Helv. Chim. Acta*, 1923, **6**, 1091). The resulting acid was repeatedly crystallised from acetone–benzene and melted at 224°. Analysis of the silver salt (Found: Ag, 61·3. Calc. for $C_9H_3O_6Ag_3$: Ag, 61·0%) indicated that the acid was one of the benzenetricarboxylic acids. Of these, hemimellitic acid is eliminated by its melting point (190°), and trimesic acid (m. p. 380°) ıt, by the fact that the acid obtained from dipinene gave a fluorescent id ...duct on condensation with resorcinol. Somewhat discordant quent ... ranging from 216—218° (Schultz, *Annalen*, 1908, **359**, 129;

Aschan and Virtanen, *ibid.*, 1921, **424**, 213) to 230° (von Braun, Kirschbaum, and Schuhmann, *Ber.*, 1920, **53**, 1164), have been given as the melting point of trimellitic acid.

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CCCCX.—*The Reduction of Nitro-compounds by Aromatic Ketols. Part II. Some* o-, m-, *and* p-*Azoxy-compounds.*

By HUGH BRYAN NISBET.

IN extending the work already done (Part I, J., 1927, 2081), it has been proved that benzoin and its homologues in hot alcoholic solution under the influence of a trace of sodium ethoxide reduce nitro-groups to azoxy-groups no matter what position these occupy in the benzene ring. Whilst the reaction, as a method of preparing azoxy-compounds, still continues to be particularly successful in the case of para-compounds and more particularly in the case of para-compounds containing a carbon-to-carbon or a carbon-to-nitrogen double bond, yields of the order 50—87% being obtained, it is not so successful in the case of *o*- and *m*-compounds, the yields dropping to the order of 6—50%.

The isolation of the azoxy-compound from the accompanying diketone is the main difficulty, for only methods of fractional crystallisation can be resorted to because azoxy-compounds readily decompose when distilled, even in a vacuum, especially when in admixture with other compounds. *p*-Azoxy-compounds are usually much less soluble in common solvents than benzil and can, in general, be easily separated even in alcoholic solution. *o*- and *m*-Azoxy-compounds, however, are as soluble as or more soluble than the diketone, which is often the first product of the reaction, whilst the azoxy-compound must be isolated from the mother-liquors. In many cases it has been found impossible to isolate the azoxy-compound; but in every case examined it has been possible to separate the diketone and thus prove that the nitro-group has oxidised the ketol and has at the same time suffered reduction. This reaction is utilised in a new preparation of anisil and furil by oxidation of the corresponding ketol with nitrobenzene.

o-, *m*-, and *p*-Azoxy-compounds have been prepared from *o*-, *m*-,

and *p*-nitrobenzylideneacetophenone, 2-*o*-, 2-*m*-, and 2-*p*-nitrostyryl-3-methylchromone, and *o*-, *m*-, and *p*-nitrobenzylidene-*p*-bromoaniline. *p*-Azoxybenzylidene-*p*-toluidine has already been described (J., 1927, 2084); the m-*azoxy*-compound has now been prepared, but the o-azoxy-compound could not be isolated. Ethyl *p*-nitrobenzoate is reduced to ethyl *p*-azoxybenzoate, but the isolation of the esters of *m*-and o-azoxybenzoic acids could not be accomplished. The preparation of *o*- and *m*-azoxybenzonitrile, of azoxybenzene, and of α-azoxynaphthalene (compare Cumming and Steele, J., 1923, **123**, 2466) failed. In each case, however, benzil was separated.

EXPERIMENTAL.

Preparation of 2-Nitrostyryl-3-methylchromones.—2 : 3-Dimethylchromone was condensed with the corresponding nitrobenzaldehyde by Heilbron, Barnes, and Morton's method (J., 1923, **123**, 2565).

2-o-*Nitrostyryl-3-methylchromone*, $C_6H_4 {<}\begin{matrix} CO{\cdot}CMe \\ O{-}C{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2 \end{matrix}$. 2 : 3-Dimethylchromone (2·8 g.) and *o*-nitrobenzaldehyde (2·2 g.) gave 1·6 g. of a solid which recrystallised from glacial acetic acid in yellow needles, m. p. 161° (Found : N, 4·5. $C_{18}H_{13}O_4N$ requires N, 4·55%).

2-m-*Nitrostyryl-3-methylchromone.* The chromone (3·4 g.) and *m*-nitrobenzaldehyde (3 g.) gave a solid which recrystallised from acetone in greenish-yellow needles (3 g.), m. p. 212° (Found : N, 4·55%).

2-p-*Nitrostyryl-3-methylchromone*, similarly prepared from *p*-nitrobenzaldehyde (3 g.), crystallised from glacial acetic acid in orange-yellow needles (2·8 g.), m. p. 238° (Found : N, 4·5%).

Preparation of Azoxy-compounds. General Method and Remarks.—The general method described in Part I (*loc. cit.*) was again employed. In those cases in which the azoxy-compound did not separate immediately or on standing for some time, some of the alcohol was distilled off and the reaction mixture was again kept until needles of benzil crystallised. These were filtered off and the mother liquor was poured into water. The solid which separated (a mixture of benzil and azoxy-compound) was then dried and dissolved in the minimum quantity of benzene or xylene, and the azoxy-compound precipitated by addition of light petroleum.

A modification of the process, with benzene as a solvent and piperidine as an activator, was used in the preparation of 2-nitro-azoxytoluene.

Azoxybenzylideneacetophenone, $(C_6H_5{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4)_2N_2O$ ...benzylideneacetophenone (4·2 g.) and benzoin (5·4 g.) gave ...7% of the theoretical yield) of the *p*-azoxy-compound

which recrystallised from xylene in yellow flakes, m. p. 211—213° (compare Vorländer, *Ber.*, 1906, **39**, 810) (Found : N, 5·8. Calc. : N, 6·1%).

m-*Azoxybenzylideneacetophenone*. *m*-Nitrobenzylideneacetophenone (4·8 g.) and benzoin (6·5 g.) gave an oily solid which crystallised after some time. Recrystallised from dilute acetone and finally purified by dissolution in hot xylene and precipitation with light petroleum, it gave a brown, microcrystalline solid, m. p. 156—157°. Yield, 0·75 g. (6%) (Found : N, 6·1. $C_{30}H_{22}O_3N_2$ requires N, 6·1%).

o-*Azoxybenzylideneacetophenone*. *o*-Nitrobenzylideneacetophenone (4·6 g.) and benzoin (6·36 g.) gave benzil (4·5 g.) as a first product, and the mother-liquor, poured into water, gave a brown solid which crystallised from benzene and light petroleum in brown flakes, m. p. 141—142° after softening at 135°. Yield, 1·2 g. (11%) (Found : N, 6·2%).

2-p-*Azoxystyryl*-3-*methylchromone*. 2-*p*-Nitrostyryl-3-methylchromone (1·5 g.) and benzoin (1·1 g.) gave 0·6 g. (43%) of the p-*azoxy*-compound, which recrystallised from xylene in orange-yellow flakes, m. p. 289° (Found : N, 5·0. $C_{36}H_{26}O_5N_2$ requires N, 4·9%).

2-m-*Azoxystyryl*-3-*methylchromone* (0·75 g.; 62%), prepared from 2-*m*-nitrostyryl-3-methylchromone (1·3 g.) and benzoin (1·2 g.), separated from xylene as a *yellowish-white, microcrystalline solid*, m. p. 275·5° (Found : N, 5·0%).

2-o-*Azoxystyryl*-3-*methylchromone* (0·2 g.; 15%), obtained from 2-*o*-nitrostyryl-3-methylchromone (1·5 g.) and benzoin (1·3 g.), formed greenish-yellow needles, m. p. 202° (Found : N, 4·8%).

p-*Azoxybenzylidene*-p-*bromoaniline*, $(C_6H_4Br{\cdot}N{:}CH{\cdot}C_6H_4)_2N_2O$, (1 g.; 55%), prepared from *p*-nitrobenzylidene-*p*-bromoaniline (2 g.) and benzoin (2 g.), recrystallised from glacial acetic acid in yellowish-red plates, m. p. 218° (Found : N, 10·15. $C_{26}H_{18}ON_4Br_2$ requires N, 10·0%).

m-*Azoxybenzylidene*-p-*bromoaniline*. m-*Nitrobenzylidene*-p-*bromoaniline* was prepared by heating *m*-nitrobenzaldehyde and *p*-bromoaniline together until no more water was given off. It crystallised from alcohol in long, yellow needles, m. p. 84° (Found : N, 9·4. $C_{13}H_9O_2N_2Br$ requires N, 9·2%).

m-Nitrobenzylidene-*p*-bromoaniline (4 g.) and benzoin (4 g.) gave on standing for some time 0·7 g. (19%) of the m-*azoxy*-compound, which separated from benzene and light petroleum as a yellow, microcrystalline solid, m. p. 120° (Found : N, 10·15. $C_{26}H_{18}ON_4Br_2$ requires N, 10·0%).

o-*Azoxybenzylidene*-p-*bromoaniline* (0·5 g.; 27%), obtained from

o-nitrobenzylidene-*p*-bromoaniline (2 g.) and benzoin (2 g.) after standing for 2 days, crystallised from xylene and light petroleum in yellow needles, m. p. 299° (Found : N, 10·3%).

m-*Azoxybenzylidene*-p-*toluidine* (2 g.; 46%), obtained from *m*-nitrobenzylidene-*p*-toluidine (4·8 g.) and benzoin (5 g.) after standing for some time, was recrystallised, first from glacial acetic acid and then from benzene and light petroleum; it formed pale yellow needles, m. p. 150° after softening at 135° (Found : N, 13·0. $C_{28}H_{24}ON_4$ requires N, 13·0%).

Ethyl *p*-azoxybenzoate (2·75 g.; 78%), prepared from ethyl *p*-nitrobenzoate (4 g.) and benzoin (6·5 g.), crystallised from glacial acetic acid in salmon-pink needles, m. p. 117° (compare Meyer and Dahlem, *Annalen*, 1903, **326**, 334) (Found : N, 8·3. Calc. : N, 8·2%).

2-*Nitro*-3-*azoxytoluene*. A solution of 2 : 4-dinitrotoluene (5 g.) and benzoin (10 g.) in 15 c.c. of benzene containing 2 c.c. of piperidine was boiled under reflux for 6 hours. The solvent was then allowed to evaporate almost to dryness. The solid which separated, after being washed with a little cold benzene and recrystallised from glacial acetic acid and from benzene–light petroleum, formed yellowish-white needles, m. p. 164° (compare Brand and Zöller, *Ber.*, 1907, **40**, 3329). Yield, 1 g. (23%) (Found : N, 17·6. Calc. : N, 17·7%).

Preparation of Anisil and Furil.—Although azoxybenzene could not be isolated in the reduction of nitrobenzene by means of benzoin, anisoin, or furoin, by using excess of the oxidising agent it was found possible to utilise the reaction as a method of preparing anisil and furil in 80% and 90% yields, respectively. Benzil is obtained by the same reaction in yields of 30—40%.

A solution of the ketol (5 g.) and nitrobenzene (4 g.) in 50 c.c. of alcohol containing 2 c.c. of 6% alcoholic sodium ethoxide was boiled under reflux for 2—3 minutes and then allowed to cool. The diketone which separated, recrystallised from alcohol, gave 4 g. of anisil, m. p. 133°, in the case of anisoin, and 4·7 g. of furil, m. p. 162°, in the case of furoin.

The author again desires to thank Prof. A. A. Boon for his interest in the work and for providing facilities for its prosecution.

Heriot-Watt College, Edinburgh. [*Received, October 8th*, 1928.]

CCCCXI.—*Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part II. Mechanism of Exhaustive Methylation* (continued).

By Christopher Kelk Ingold and Charles Cyril Norrey Vass.

In Part I,* a theory of the mechanism of the decomposition of quaternary ammonium compounds was developed and shown to be in accord with several different types of experimental data. One of the tests applied consisted in tracing the relation between the constitution of an alkyl group (Alk) and the ratio of the olefin formed to the methyl alcohol eliminated in the decomposition of the corresponding trimethylalkylammonium hydroxide ($\mathrm{Alk{\cdot}NMe_3{\cdot}OH}$). Expanding Alk to $\mathrm{CHR^1R^2{\cdot}CR^3R^4{\cdot}}$, and naming the simultaneous reactions referred to (*A*) and (*B*) for convenience in reference :

$$\mathrm{{}^{R^1}_{R^2}{>}CH{-}\underset{R^4}{\overset{R^3}{C}}{-}\overset{\oplus}{N}Me_3\}\overset{\ominus}{O}H} \rightarrow \mathrm{{}^{R^1}_{R^2}{>}C{=}C{<}^{R^3}_{R^4} + NMe_3 + H_2O} \quad . \quad (A)$$

$$\rightarrow \mathrm{{}^{R^1}_{R^2}{>}CH{\cdot}CR^3R^4{\cdot}NMe_2 + MeOH} \quad . \quad (B)$$

theory predicted that the suppression of (*A*) in favour of (*B*)

(i) should be governed by R^1 and R^2 much more than by R^3 and R^4.

(ii) should increase, tending towards constancy, with increasing R^1 and R^2.

(iii) should be greater when $\mathrm{R^1R^2CH{\cdot}}$, or any part thereof, is branched than when the corresponding group or part is unbranched but isomeric.

In Part I, prediction (i) was established very fully, (ii) was demonstrated for groups up to and including propyl, and (iii) was confirmed for *n*- and *iso*-propyl. In the present paper, this particular test of the general theory is extended, prediction (ii) is verified up to and including hexyl, and (iii) is further established in the case of *n*- and *iso*-butyl. The results are shown in Table I.

Since the publication of Part I, the technique of these decompositions has been improved in various minor details (*e.g.*, the quantitative collection of the olefin and the more complete exclusion of carbonates and silicates from the hydroxide solution) and we have accordingly to correct the earlier values for propyl and butyl by a

* The parent paper of this series (Hanhart and Ingold, J., 1927, 997), herein called Part I, was actually published under another (more general) title.

TABLE I.

Decomposition of Trimethylalkylammonium Hydroxides,
$\{Alk{\cdot}NMe_3\}^{\cdot}OH'$ or $\{CHR^1R^2{\cdot}CR^3R^4{\cdot}NMe_3\}^{\cdot}OH'$.

			Mols. % olefin (reaction A)		
			Previous results.		This pap(er)
No.	Alk.	$R^1(R^2=R^3=R^4=H)$.	H. & I.*	v. B.†	(see Table II
1	Ethyl	H·	—	—	95
2	*n*-Propyl	CH_3·	81	—	84
3	*n*-Butyl	$CH_3{\cdot}CH_2$·	75	50	79
4	*n*-Amyl	$CH_3{\cdot}CH_2{\cdot}CH_2$·	—	40	77
5	*n*-Hexyl	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$·	—	27	76
6	*n*-Heptyl	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$·	—	25	74
7	*n*-Octyl	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$·	—	26	75
8	*iso*Amyl	$(CH_3)_2CH$·	—	—	72

* *Hanhart and Ingold, Part I, loc. cit.*
† von Braun, *Annalen*, 1911, **382**, 1.

few units per cent.* Although it is necessary to direct attention t the results already on record (Table I), we do not propose here t discuss the cause of the large discrepancies between v. Braun' results and those obtained by us, since this point, which is of con siderable interest, will be dealt with in a forthcoming paper by tha author. The figures in the last column of the table we regard wit confidence. In Nos. 1—7 the suppression of (*A*) with increasing R^1 and the approach to a constant value (75%) are clearly indicate (prediction ii), and the comparison of Nos. 4 and 8, in which CHR^1R^2 is *n*- and *iso*-butyl, respectively, supplies a further confirmation o (iii).

EXPERIMENTAL.

The quaternary compounds were prepared from trimethylamin and the appropriate alkyl bromide or iodide. Benz-*n*-amylamid (an intermediate in the preparation of *n*-amyl bromide from piperi dine) is described by v. Braun and Sobechi as an oil (*Ber.*, 1910, **43** 3596). Our specimens were in all cases solid and crystallised fron ether–ligroin in needles, m. p. 31—32°, b. p. 205—210°/18 mm.

The method was substantially the same as in Part I, the olefin being weighed as their dibromides (Table II, column 5), and th mixed tertiary bases analysed as their methopicrates. Since th precipitation of these was never complete (Table II, column 7), th compositions deduced from their nitrogen content constitute only an approximate check (Table II, column 8). The hexene, heptene, and octene were collected in chloroform (under hydrochloric acid) and subsequently combined with bromine.

* There is theoretical reason to suspect that the proportion of olefin formed would vary *slightly* with the form of the apparatus used for distillation, so that the 3—4% difference may not all represent experimental error.

TABLE II.

Expt. No.	Alkyl group (Alk).	Salt taken (anion).	Wt. converted into hydroxide.	Olefin formed. Mols. %.	Olefin formed. Mean.	Yield of methopicrates.	Trimethylamine (mols.%).
24	Ethyl	Bromide	32·76	94·5		—	—
25	,,	*Iodide*	39·17	94·8	94·6	93·2	*Almost*
26	,,	,,	31·14	94·4		92·7	pure *
20	*n*-Propyl	Iodide	25·89	82·9		—	—
21	,,	,,	40·05	84·1	83·7	91·7	88
22	,,	,,	37·87	84·2		85·0	93
5	*n*-Butyl	*Iodide*	38·43	79·6		89·1	80
6	,,	,,	42·46	80·0	79·2	80·0	84
7	,,	,,	41·10	77·9		79·2	82
27	*n*-Amyl	Bromide	21·72	77·0	76·6	89·4	80
28	,,	,,	25·97	76·1		92·8	80
29	*n*-Hexyl	Iodide	25·06	75·6	75·6	90·2	78
17	*n*-Heptyl	Iodide	20·76	74·7		—	—
18	,,	,,	37·43	73·0	73·8	95·4	75
19	,,	,,	40·09	73·6		—	—
12	*n*-Octyl	Iodide	27·36	73·9		—	—
13	,,	,,	42·55	76·7	75·4	—	—
14	,,	,,	43·85	74·8		94·6	78
15	,,	,,	38·71	76·0		—	—
8	*iso*Amyl	Bromide	26·23	71·5		—	—
9	,,	,,	37·41	72·2	71·7	94·4	76
10	,,	,,	37·50	71·6		—	—

* The compositions of the constituents are here too close for analysis to be of service.

We wish to express our thanks to the Royal Society for a grant in aid of this investigation.

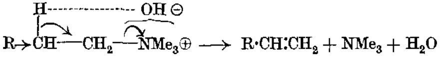
THE UNIVERSITY, LEEDS. [*Received, October 26th*, 1928.]

CCCCXII.—*Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part III. A Decomposition of Dialkylsulphones.*

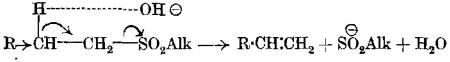
By GEOFFREY WILLIAM FENTON and CHRISTOPHER KELK INGOLD.

THE mechanism advanced in Part I (Hanhart and Ingold, J., 1927, 997) for the decomposition of quaternary ammonium hydroxides into olefins, tertiary amines, and water suggests that dialkylsulphones (Alk·SO_2·Alk′) should be capable of a similar decomposition, since the dipole in the sulphone group (Sugden, Reed, and Wilkins, J., 1925, **127**, 1525; Sugden, this vol., p. 263) would be expected to induce incipient ionisation in the β-protons of each alkyl group in sufficient degree to facilitate their union with a suitable proton-

acceptor. The products would be an olefin and an alkylsulphinic acid (*A*). Indeed the suggested analogy between



and



is complete except in two respects. The first of these is that, whereas the quaternary ammonium compound can supply its own proton-seeking anions (hydroxide), the sulphone cannot; wherefore alkali would have to be added in the latter case (*B*). The second is that the electron-affinity of $\cdot SO_2Alk$ is weaker than that of $\cdot NMe_3$ (Ingold, Ingold, and Shaw, J., 1927, 813); wherefore the effect of R→ in inhibiting the reaction (compare Parts I and II) should work more powerfully in the case of the sulphones (*C*). Otherwise we should expect most of the features which characterise the reaction of the quaternary hydroxides to apply without change to that of the sulphones, as, for instance, the rule regarding the preferential elimination of ethylene (*D*).

We have examined the action of alkali on three typical sulphones and have established the following facts :

(1) The expected decomposition of diethylsulphone occurs, the products being ethylene and ethanesulphinic acid (compare *A*). Alkali is necessary to the decomposition (compare *B*).

(2) *Ethyl*-n-*octylsulphone* similarly decomposes, giving ethylene and *n*-octanesulphinic acid, but no detectable quantity of *n*-octene or ethanesulphinic acid. This illustrates the ethylene rule (compare *D*).

(3) In contrast with the fission of trimethyl-*n*-octylammonium hydroxide, which yields some 75% of *n*-octene (compare Part II), di-*n*-octylsulphone is not decomposed at all under the conditions of reaction mentioned under (1) and (2); so that, when each β-proton is protected by the electron-source action of a *n*-hexyl group (R in the formulæ), the fission of the sulphone is inhibited completely (compare *C*).

EXPERIMENTAL.

Decomposition of Diethylsulphone.—Diethylsulphone (4 g., m. p. 71°, prepared from diethyl sulphide by oxidation with permanganate, and crystallised from alcohol) was mixed with ground potassium hydroxide (15 g.) and a little water, and the melt heated in a metal-at 200° until the vigorous evolution of gas ceased; the whole

apparatus was then swept out with a current of nitrogen. The gases were passed first through dilute hydrochloric acid (two flasks), then through liquid bromine (two flasks), and finally into an aspirator. The gas in this was proved to be free from ethane or other hydrocarbon. The hydrochloric acid solution was tested for ethyl alcohol by distilling it and treating the first portion of the distillate with *p*-nitrobenzoyl chloride and alkali; no ethyl *p*-nitrobenzoate was obtained. Thus it appears that possible hydrolysis to ethyl alcohol and ethanesulphinic acid does not correspond with the products, and that, if ethanesulphinic acid is formed in any manner, it does not break down to ethane and sulphurous acid under the conditions of the experiment. The contents of the traps containing bromine were mixed with ice, decolorised with sulphur dioxide, and made alkaline with sodium carbonate. The heavy oil was partly run off and partly extracted with ligroin, and then distilled, 3·7 g., b. p. 129—131°, being obtained. Its b. p. and analysis (Found : C, 12·4; H, 2·2. Calc. : C, 12·8; H, 2·1%) identify it as ethylene dibromide. The alkaline residue was mixed with water and dilute hydrochloric acid, during which process the odour of hydrogen sulphide was noticed, and then exactly neutralised with sodium carbonate and evaporated to dryness. The residue was extracted with alcohol, which removed sodium ethanesulphinate and traces of inorganic salts; and the latter were finally eliminated by complete evaporation of the alcohol and re-extraction of the sulphinate with the same solvent, from which it crystallised on concentration (yield, 60%). From the sodium salt (2·3 g.), barium ethanesulphinate was prepared by precipitation with barium iodide in alcoholic solution (Found : Ba, 42·4; C, 14·7; H, 3·1. Calc. : Ba, 42·5; C, 14·8; H, 3·1%).

Decomposition of Ethyl-n-*octylsulphone*.—Sodium (1·2 g.) was dissolved in a solution of ethyl mercaptan (3·1 g.) in ether and the ether evaporated. The residue was heated on the steam-bath for 5 hours with an alcoholic solution of *n*-octyl bromide (10 g.) and the product was poured into a large volume of water and extracted with ether. The ethyl *n*-octyl sulphide, b. p. 102—103°/11 mm., was run with rapid stirring into nitric acid, and the product poured on ice; a rapidly solidifying oil was then precipitated. On crystallisation from ligroin this yielded *ethyl*-n-*octylsulphone* as platelets, m. p. 68°. On one occasion the product obtained by oxidation with nitric acid remained largely liquid; it was therefore treated with powdered potassium permanganate in glacial acetic acid and the same crystalline sulphone, m. p. 68°, was obtained (Found : C, 58·4; H, 10·9. $C_{10}H_{22}O_2S$ requires C, 58·3; H, 10·7%).

The method of decomposition was that already described for diethylsulphone and the reaction again took place smoothly at 200°;

the bath, however, was raised to 270° at the end of the process. The absence of appreciable amounts of ethane, octane, ethyl alcohol, and octyl alcohol was demonstrated. Octene, which would have collected mainly in the hydrochloric acid traps, was also absent, and the bromine solution, on being worked up for bromohydrocarbons, yielded only ethylene dibromide (b. p. 129—131°. Found: C, 13·3; H, 2·4%). The alkaline residues on acidification had an odour of hydrogen sulphide, and, following the procedure described above, sodium *n*-octanesulphinate was isolated in 70% yield. The corresponding *ferric* salt was obtained by precipitation with ferric chloride in the presence of dilute hydrochloric acid (Found: Fe, 9·6. $C_{24}H_{51}O_6S_3Fe$ requires Fe, 9·5%).

Stability of Di-n-octylsulphone.—A portion (180 c.c.) of a solution of potassium hydroxide (17 g.) in ethyl alcohol (450 c.c.) was saturated with hydrogen sulphide and added to the remainder. *n*-Octyl bromide (20 g.) was added and the mixture was kept at the ordinary temperature for 2 days, heated for 2 hours on the steam-bath, poured into a large volume of water, and extracted with ether. The di-*n*-octyl sulphide (compare Möslinger, *Annalen*, 1877, **185**, 59), b. p. 180°/10 mm., was treated (10 g.) with nitric acid (50 c.c., *d* 1·49). The oil which was precipitated by the addition of water partly solidified on keeping, and probably consisted of a mixture of di-*n*-octyl sulphoxide and di-*n*-octylsulphone. On treatment with powdered potassium permanganate in glacial acetic acid, it yielded *di*-n-*octylsulphone*, which was isolated by adding water and passing sulphur dioxide, and was purified by crystallisation from ligroin, from which it separated in platelets, m. p. 76° (Found: C, 65·9; H, 12·0. $C_{16}H_{34}O_2S$ requires C, 66·2; H, 11·8%).

On treatment with alkali under the conditions of the previous experiments, no decomposition took place, and some unchanged sulphone collected in the first trap containing hydrochloric acid. The sulphone was therefore heated for 2 hours under reflux with 90% potassium hydroxide; again no evidence of decomposition was observed and, on cooling, the original sulphone was recovered in almost the theoretical quantity.

We wish to express our thanks to the Chemical Society for a grant in aid of this work, which is being continued.

THE UNIVERSITY, LEEDS. [*Received, October 26th*, 1928.]

CCCCXIII.—*Heterocyclic Compounds containing Arsenic. Part IV. Carbamido-derivatives of Arylarsinic Acids.*

By Ralph William Ewart Stickings.

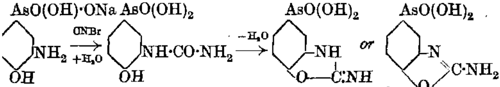
In an attempt to prepare some guanidine derivatives of aromatic arsinic acids, the well-known reaction between a primary amine and a cyanogen halide was employed :

$$R{\cdot}NH_2 + CNBr \longrightarrow R{\cdot}NH{\cdot}CN + HBr.$$
$$R{\cdot}NH{\cdot}CN + R{\cdot}NH_2,HBr \longrightarrow (R{\cdot}NH)_2C{:}NH,HBr.$$

p-Arsanilic acid and cyanogen bromide, however, would *not* react in presence of benzene, even when boiling. Sodium *p*-arsanilate reacted rapidly with an aqueous suspension of cyanogen bromide in the cold, yielding, not a guanidine derivative, but p-*carbamidophenylarsinic acid*; of the two g.-mols. of arsanilate employed, one was recovered unchanged :

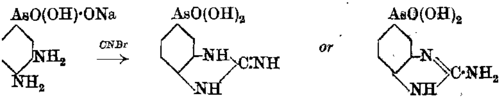
$$NH_2{\cdot}C_6H_4{\cdot}AsO(OH){\cdot}ONa + CNBr + H_2O = NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}AsO(OH)_2 + NaBr.$$

No intermediate cyanamide derivative could be isolated, and it was subsequently found that this reaction was a general one with aminoarylarsinic acids. In cases where the primary amino-group is in the ortho-position to another reactive constituent group, *e.g.*, (OH) or (NH_2), the reaction proceeds further with ring formation :



(I.)

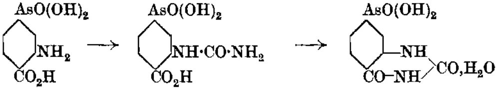
Similarly



(II.)

These heterocyclic compounds are soluble in mineral acids and in alkalis. They probably contain a primary amino-group, since, on diazotisation and boiling, the compound (I) yields a hydroxy-derivative. With compound (II), however, the reaction appeared to go further, the only product isolated being the original diaminophenylarsinic acid.

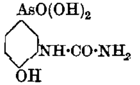
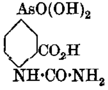
If the parent arsinic acid contains a carboxyl group ortho to the amino-group, a compound is produced by the action of cyanogen bromide and water which has the properties of a diketotetrahydroquinazoline. It is insoluble in mineral acids, is not decomposed by prolonged heating with concentrated sodium hydroxide solution or 50% sulphuric acid, and on reduction with sodium hydrosulphite gives an arseno-compound insoluble in sodium hydroxide solution. On the other hand, analysis gives figures which indicate the presence of an extra molecule of water, which cannot be removed by prolonged drying in a vacuum at 110°. It appears, therefore, that this molecule of water is attached to one of the carbonyl groups in the heterocyclic nucleus and that the reaction may be represented thus :



(III.) (IV.)

It is inconceivable that prolonged boiling with concentrated alkali solution or acid would fail to liberate ammonia and carbon dioxide from a substituted carbamide of the type (III).

Methods (Farbwerke vorm. Meister, Lucius, & Brüning, U.S.P. 1077462, D.R.-P. 213155) for the preparation of carbamidoarylarsinic acids by the potassium cyanate method lead, according to their authors, to simple carbamide derivatives such as (V) and (VI).

(V.)   (VI.)

This work has been confirmed in the case of (V); the compound isolated differs in properties, as would be expected, from the condensation product (I) obtained by means of cyanogen bromide.

Further work is in progress to elucidate the course of the reaction which produces these heterocyclic arsinic acids, as it has been found difficult to convert (V) into (I) by formation of the heterocyclic nucleus. An attempt is also being made to synthesise (IV) by introducing the arsinic acid group at the final stage by the Bart method.

The trypanocidal action of these compounds and of further derivatives thereof has been studied and will be reported elsewhere.

EXPERIMENTAL.

p-*Carbamidophenylarsinic Acid* (compare D.R.-P. 213155).—A solution of 108 g. of *p*-arsanilic acid in aqueous sodium hydroxide (20 g. in 500 c.c. of water) and a freshly prepared suspension of 106 g. of cyanogen bromide in 300 c.c. of water were mixed and stirred; a crystalline precipitate gradually formed and the odour of cyanogen bromide disappeared. Next day, the mixture was acidified to Congo-red with concentrated hydrochloric acid. The precipitate was collected, redissolved in aqueous sodium hydroxide, and, after the solution had been made neutral and treated with charcoal, re-precipitated with hydrochloric acid; yield, 89 g. (Found: As, 28·7; N, 10·8. $C_7H_9O_4N_2As$ requires As, 28·8; N, 10·8%). The product crystallised from hot water in glistening needles. It was sparingly soluble in cold water or organic solvents, insoluble in dilute mineral acids, and readily soluble in hot water and in caustic alkali or alkali carbonate solutions. Warming with sodium hydroxide solution liberated ammonia, and the solution on acidification with acetic acid gave carbon dioxide and *p*-arsanilic acid.

5-*Carbamido-2-hydroxyphenylarsinic Acid*.—5-Amino-2-hydroxyphenylarsinic acid (Fourneau, Tréfouel, and Bénoit, *Bull. Soc. chim.*, 1927, **41**, 449) (117 g.) was treated exactly as described above with 106 g. of cyanogen bromide. The product obtained on acidification was decolorised by isolation of the sodium salt and regeneration of the acid. Yield, 64 g. of white, needle-shaped crystals, soluble in hot water and in alkalis, insoluble in mineral acids (Found: As, 27·0; N, 10·3. $C_7H_9O_5N_2As$ requires As, 27·2; N, 10·1%).

1-*Aminobenzoxazole*-4-*arsinic Acid* (I).—The reaction between 3-amino-4-hydroxyphenylarsinic acid (117 g., dissolved in a solution of 20 g. of sodium hydroxide in 500 c.c. of water) and 120 g. (excess) of cyanogen bromide was complete in about 1 hour. After the addition of 10 c.c. of glacial acetic acid, the rather dark precipitate was collected and dissolved in 20% sodium hydroxide solution, which was then cooled and treated with an excess of sodium chloride. Next day, the thick mass of crystals obtained was washed with brine and decolorised in 400 c.c. of hot water with charcoal. Acidification with excess of acetic acid gave 88 g. of white prismatic needles (Found: As, 28·9; N, 10·7. $C_7H_7O_4N_2As$ requires As, 29·1; N, 10·8%).

The new *acid* is soluble in dilute mineral acids and in alkalis and sparingly soluble in hot or cold water. It is only slowly decomposed by boiling concentrated aqueous caustic alkali.

2-*Aminobenziminazole*-5-*arsinic Acid* (II).—3 : 4-Diaminophenyl-

arsinic acid (Bertheim, *Ber.*, 1911, **44**, 3095) (116 g.) was treated exactly as described in the preceding preparation. The *product*, also purified in the same way, formed white, slender needles (55 g.), moderately easily soluble in hot water and readily soluble in dilute mineral acids or alkalis (Found : As, 29·0; N, 16·1. $C_7H_8O_3N_3As$ requires As, 29·2; N, 16·3%).

1-*Amino*-6-*acetamidobenzoxazole*-4-*arsinic Acid*.—A neutral solution of 28 g. of 3-amino-5-acetamido-4-hydroxyphenylarsinic acid (this vol., p. 2376) in dilute aqueous sodium hydroxide was diluted to 150 c.c. and added rapidly to an aqueous suspension of cyanogen bromide freshly made from 18 g. of bromine, and the whole was well stirred. After 1 hour, the product was acidified with acetic acid in excess and the brown crystals obtained were treated in alkali solution with charcoal and reprecipitated as white, prismatic needles (20 g.), readily soluble in dilute mineral acids and in alkalis (Found : As, 23·2; N, 13·2. $C_9H_{10}O_5N_3As$ requires As, 23·8; N, 13·3%).

2 : 4-*Diketo*-1 : 2 : 3 : 4-*tetrahydro*-1 : 3-*quinazoline*-7-*arsinic Acid* (IV).—3-Amino-4-carboxyphenylarsinic acid (26 g.) in neutral solution was similarly treated with cyanogen bromide (from 15 g. of bromine) and left for 1 hour in a warm place. The crystalline precipitate obtained on acidification (to Congo-red) with hydrochloric acid was recovered, after the usual purification with charcoal, in white prisms (18 g.), which were dried at 110° (Found : As, 24·4; N, 9·3. $C_8H_7O_5N_2As$ requires As, 26·2; N, 9·8%. $C_8H_7O_5N_2As,H_2O$ requires As, 24·7; N, 9·2%).

The author's thanks are due to Messrs. May & Baker Ltd., Battersea, for permission to publish this work.

THE RESEARCH LABORATORIES, MESSRS. MAY & BAKER, LTD., WANDSWORTH, S.W. 18. [*Received, October 18th*, 1928.]

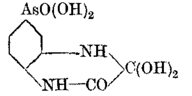
CCCCXIV.—*Heterocyclic Compounds of Arsenic. Part V. Benziminazolearsinic Acids.*

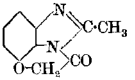
By MONTAGUE ALEXANDRA PHILLIPS.

IT has previously been shown (Phillips, this vol., pp. 172, 2393) that 2-substituted benziminazoles can readily be obtained from mono- and di-acyl-*o*-diamines by the action of boiling dilute mineral acids and from *o*-diamines by the action of organic acids in the presence of boiling dilute mineral acids. It is now shown that these reactions may be employed for the synthesis of benziminazolearsinic acids. 3 : 4-Diaminophenylarsinic acid gives with formic, acetic, propionic,

and lactic acids, respectively, benziminazole-5(6)-arsinic acid, 2-methyl-, 2-*ethyl*-, and 2-α-*hydroxyethyl-benziminazole*-5(6)-*arsinic acids*. Similarly, 2-*methyl*- and 2-α-*hydroxyethyl-benziminazole*-4(7)-*arsinic acids* and *benziminazole*-4(7)-*arsinic acid* were obtained from 2 : 3-diaminophenylarsinic acid. 3 : 4-Diacetamidophenylarsinic acid, on treatment with boiling dilute hydrochloric acid, gave 2-methylbenziminazole-5(6)-arsinic acid, which was also obtained by the application of the Bart reaction to 5-amino-2-methylbenziminazole. In no case except that of 2-α-hydroxyethylbenziminazole-5(6)-arsinic acid was the cyclic compound obtained in the absence of the catalyst.

The action of dibasic acids on the above diaminophenylarsinic acids calls for special note (compare Phillips, this vol., p. 2397). Malonic acid and 3 : 4-diaminophenylarsinic acid in the presence of boiling dilute hydrochloric acid gave an amorphous compound which appeared to be malon-*o*-phenyleneamide-4-arsinic acid, identical with the substance obtained by Lewis and Bent (*J. Amer. Chem. Soc.*, 1926, **48**, 949) from 3 : 4-diaminophenylarsinic acid and malonic ester. Oxalic acid under the same conditions gave a quantitative yield of 2 : 3-*dihydroxyquinoxaline*-6(7)-*arsinic acid* identical with the product obtained in this laboratory by the reduction of 3-nitro-4-oxalylaminophenylarsinic acid and by the action of oxalyl chloride on 3 : 4-diaminophenylarsinic acid. In all cases it was obtained as a monohydrate which did not lose water at 100°. It is possibly, therefore, a dihydroxy-derivative of formula (I).

(I.) 

 (II.)

The arseno-derivative obtained by reduction of compound (I) was insoluble in alkalis and dilute mineral acids; the isomeric 2-carboxybenziminazolearsinic acid formula is therefore untenable (compare Phillips, this vol., p. 2398).

2 : 3-Diaminophenylarsinic acid condensed similarly with oxalic acid under the above conditions, giving a good yield of 2 : 3-*dihydroxyquinoxaline*-5(8)-*arsinic acid*, which was also obtained as a monohydrate stable at 100°.

The action of succinic or benzoic acid and derivatives of the latter on 3 : 4-diaminophenylarsinic acid gave no crystalline product.

Although 5-amino-3-hydroxy-1 : 4-benz*iso*oxazine and its 6-arsinic acid (Newbery and Phillips, this vol., p. 3048; Newbery, Phillips, and Stickings, *ibid.*, p. 3057) behave similarly to *o*-amino-

*acetanilide towards nitrous acid, forming triazoles, complex benz*iminazoles of the type (II) could not be obtained from them by the action of acetic anhydride and boiling dilute hydrochloric acid or from their acetyl derivatives by treatment with boiling dilute mineral acids.

Attempts to nitrate 2-methylbenziminazole-5(6)-arsinic acid under a variety of conditions gave either unchanged material or mixtures from which no crystalline substance could be obtained; similar results were recorded for 3 : 4-diacetamidophenylarsinic acid.

EXPERIMENTAL.

3 : 4-Diacetamidophenylarsinic acid could not be obtained by acetylation of 3 : 4-diaminophenylarsinic acid (compare Baxter and Fargher, J., 1919, **115**, 1372), but was prepared in 50% yield by decomposing a *diazotised solution* of 4-*amino*-1 : 2-diacetamidobenzene (Phillips, this vol., p. 175) (8 g.; 60 c.c. of ice-water; 8 c.c. of hydrochloric acid, *d* 1·16; 2·8 g. of sodium nitrite) at 50° with a copper arsenite suspension (5 g. of arsenious oxide; 6 g. of sodium hydroxide in 50 c.c. of water; 8 c.c. of 2*N*-copper sulphate). The solution was then acidified to litmus, filtered from amorphous material, acidified to Congo-red, and concentrated to 50 c.c. The arsinic acid obtained crystallised from concentrated aqueous solution in colourless needles, m. p. 320° (decomp.), readily soluble *in cold water* (Found: As, 24·0; N, 9·0. Calc.: As, 23·7; N, 8·9%).

2-Methylbenziminazole-5(6)-arsinic acid, obtained by Baxter and Fargher (*loc. cit.*) by treatment of the above arsinic acid with water in a sealed tube, was best prepared (*a*) by refluxing the above acid (4 g.) with 5*N*-hydrochloric acid (20 c.c.) for 40 minutes and neutralising the filtered solution to Congo-red; yield, 2·5 g. (78%). It was also obtained (*b*) by boiling under reflux 3 : 4-diaminophenylarsinic acid (4 g.; Bertheim, *Ber.*, 1911, **44**, 3095) with 5*N*-hydrochloric acid (30 c.c.) and acetic acid or anhydride (2 c.c.) for 40 minutes and neutralising the filtered solution to Congo-red; yield, 2 g. (40%). (*c*) A diazotised solution of 5-amino-2-methylbenziminazole dihydrochloride (22 g.; water, 100 c.c.; sodium nitrite, 7 g.) was decomposed at 50° with copper arsenite (arsenious oxide, 15 g.; sodium hydroxide, 15 g.; 2*N*-copper sulphate, 6 c.c.; water, 100 c.c.); yield, 30%.

2-Methylbenziminazole-5(6)-arsinic acid (m. p. 275°, decomp., when anhydrous) was *obtained in all cases as a monohydrate* (Found: As, 27·3; N, 10·0. Calc.: As, 27·4; N, 10·2%), which lost half its water at 100° and the rest only slowly at 120° (Found of b[illegible]hydrous substance: As, 29·4; N, 10·8. Calc.: As, 29·3; may be %). It consists of colourless prisms, sparingly soluble in

3 : 4-Diam[illegible]

cold water, but readily soluble in mineral acids and in alkalis. The calcium and magnesium salts are amorphous. The acid contains no free amino-group as shown by the diazo-alkaline β-naphthol test. The *nitrate* (Found: As, 24·0. N, 13·45. $C_8H_9O_3N_2As,HNO_3$ requires As, 23·5; N, 13·2%) was obtained in white needles in quantitative yield by the action of boiling 10% nitric acid on the arsinic acid.

2 : 2'-*Dimethyl*-5 : 5'-*arsenobenziminazole*, obtained in 60% yield by hyposulphite reduction of the above arsinic acid, was a deep yellow, amorphous solid, insoluble in water and alkalis, soluble in dilute mineral acids. It contains no free amino-group as shown by the diazo-alkaline β-naphthol test. On desiccation in a vacuum it retained 4 molecules of water, one of which was removed with difficulty at 90° (Found: As, 32·0; N, 11·85; H_2O lost at 90°, 3·9. $C_{16}H_{14}N_4As_2,4H_2O$ requires As, 31·0; N, 11·6; $1H_2O$, 3·95%).

The following three acids were obtained by refluxing 3 : 4-diaminophenylarsinic acid with 5*N*-hydrochloric acid and formic, propionic, or *l*-lactic acid for 1 hour, treating the solution with charcoal, and neutralising it to Congo-red or litmus.

Benziminazole-5(6)-arsinic acid crystallised from water in diamond-shaped plates, identical with the material obtained by Baxter and Fargher's method (*loc. cit.*) (Found: As, 31·2; N, 11·6. Calc.: As, 31·0; N, 11·6%). On reduction with sodium hyposulphite, it gave 5 : 5'-*arsenobenziminazole* in 60% yield as a yellow amorphous solid, insoluble in water, alkalis, and organic solvents, soluble in dilute mineral acids, and containing no free amino-group (Found: As, 38·6; N, 14·4. $C_{14}H_{10}N_4As_2$ requires As, 39·0; N, 14·6%).

2-*Ethylbenziminazole*-5(6)-*arsinic acid* was purified by the method suggested by Christiansen (*J. Amer. Chem. Soc.*, 1920, **42**, 2403) for 3-amino-4-hydroxyphenylarsinic acid. It formed clusters of needles, moderately easily soluble in cold water and alcohol, readily soluble in alkalis and dilute mineral acids. The calcium salt separates from a hot aqueous solution in clusters of prisms, soluble in cold water; the magnesium salt is amorphous (Found: As, 27·5; N, 10·5. $C_9H_{11}O_3N_2As$ requires As, 27·8; N, 10·4%).

2-α-*Hydroxyethylbenziminazole*-5(6)-*arsinic acid*, purified by acidification of its alkaline solution, formed colourless needles, insoluble in cold water and sparingly soluble in boiling water. It forms an amorphous magnesium salt (Found: As, 26·4; N, 10·0. $C_9H_{11}O_4N_2As$ requires As, 26·2; N, 9·8%). The acid was also obtained (yield, 1 g. or 40%) when 3 : 4-diaminophenylarsinic acid (2 g.) was heated in a boiling water-bath for 1 hour with *l*-lactic acid (5 c.c.), and the solution then diluted with water (30 c.c.) (Found: As, 26·0%).

2 : 3-Diaminophenylarsinic acid has been obtained (D.R.-P. 256343) by reduction of 2-nitro-3-aminophenylarsinic acid. That required for this investigation was, however, prepared as follows: 2-Nitro-3-carbethoxyaminophenylarsinic acid (5 g.) (Newbery, Phillips, and Stickings, this vol., p. 3053) was dissolved without cooling in a solution of sodium hydroxide (5 g.) in water (25 c.c.), and glucose (4 g.) was added immediately. A reaction occurred during which no ammonia was liberated. When this had subsided, the liquid was boiled for 5 minutes, acidified strongly to Congo-red, treated with charcoal, and filtered. On neutralisation to Congo-red with 10*N*-sodium hydroxide and cooling, the diamino-acid separated (yield, 1·5 g. or 45%). Purified by Christiansen's method (*loc. cit.*), it consisted of colourless plates, m. p. 198° (decomp.), sparingly soluble in water. The calcium, barium, and magnesium salts are relatively soluble and the acid gives a rich red colour with acidified dichromate solution. It differs considerably from the isomeric 3 : 4-diaminophenylarsinic acid, which gives a characteristic insoluble calcium salt (plates), decomposes at 158°, and gives a purple colour with acidified dichromate solution. This acid, moreover, is considerably more basic than 2 : 3-diaminophenylarsinic acid. The orientations of the latter acid, which is undoubtedly an *o*-phenylenediamine derivative, and of 2-nitro-3-carbethoxyaminophenylarsinic acid would therefore appear to be firmly established. *Benziminazole*-4(7)-*arsinic acid*, obtained from 2 : 3-diaminophenylarsinic acid and formic acid as described under benziminazole-5(6)-arsinic acid, forms colourless prisms, m. p. 277° (decomp.), from boiling water, in which it is sparingly soluble (Found: As, 30·9; N, 11·5%). It is markedly amphoteric, but appears to be somewhat less basic than the 5(6)-arsinic acid. The calcium salt is amorphous, and soluble in cold but insoluble in boiling water; the magnesium salt forms clusters of colourless prisms. 4 : 4′-*Arsenobenziminazole* is an amorphous yellow solid (Found in substance dried at 100°: As, 38·8; N, 14·5%), insoluble in water, alkalis and organic solvents, but soluble in dilute hydrochloric acid to give a hydrochloride, which is precipitated by excess of the mineral acid.

2-*Methylbenziminazole*-4(7)-*arsinic acid*, obtained in 50% yield from 2 : 3-diaminophenylarsinic acid and acetic anhydride in the presence of boiling 4*N*-hydrochloric acid, forms anhydrous needles, m. p. 280—282°, from boiling water (Found: As, 28·9; N, 10·7%). It is readily soluble in alkalis and dilute mineral acids. Its magnesium and calcium salts are amorphous.

2 : 2′-*Dimethyl*-4 : 4′-*arsenobenziminazole* is a yellow, amorphous solid, resembling its lower homologue in all its properties. It can

readily be dried in a vacuum, differing from 2 : 2′-dimethyl-5 : 5′-arsenobenziminazole (p. 3137) in this respect (Found: As, 36·0; N, 13·3. $C_{16}H_{14}N_4As_2$ requires As, 36·4; N, 13·6%).

*2-α-Hydroxyethylbenziminazole-*4(7)*-arsinic acid* was obtained in poor yield from 2 : 3-diaminophenylarsinic acid, *l*-lactic acid, and 4*N*-hydrochloric acid. It forms colourless needles from boiling water, is amphoteric, and gives an amorphous magnesium salt (Found: As, 26·0; N, 9·5%).

Condensation of Dibasic Acids with 2 : 3- *and* 3 : 4-*Diaminophenylarsinic Acids*.—(1) *Oxalic acid*. (a) 3 : 4-Diaminophenylarsinic acid (2 g.), 4*N*-hydrochloric acid (14 c.c.), and crystalline oxalic acid (1·2 g.) were boiled under reflux for 40 minutes. On cooling, 2 : 3-*dihydroxyquinoxaline-*6(7)*-arsinic acid* separated (yield, 1·5 g. or 60%). Crystallised many times from boiling water, in which it was very sparingly soluble, it formed colourless hexagonal plates, not molten at 300° (Found: As, 25·0; N, 9·2. $C_8H_7O_5N_2As,H_2O$ requires As, 24·8; N, 9·2%). It is insoluble in dilute mineral acids, but readily soluble in alkalis, giving with sodium hydroxide mono- and di-sodium salts. It also forms very sparingly soluble calcium, barium, and magnesium salts.

(b) 2 : 3-Diaminophenylarsinic acid, treated similarly, gave a 75% yield of 2 : 3-*dihydroxyquinoxaline-*5(8)*-arsinic acid*, which crystallised in prisms not molten at 300°. Like its isomeride, it is very sparingly soluble in boiling water and gives very sparingly soluble calcium, barium, and magnesium salts (Found: As, 24·9; N, 9·2. $C_8H_7O_5N_2As,H_2O$ requires As, 24·7; N, 9·2%). The arseno-derivative has properties identical with those of the compound derived from the isomeric 6(7)-arsinic acid.

(2) *Malonic acid*. (a) 3 : 4-Diaminophenylarsinic acid (2 g.), malonic acid (1 g.), and 4*N*-hydrochloric acid (14 c.c.), boiled under reflux for 1 hour, gave a trace only of red, amorphous material on cooling. The filtrate contained about 1 g. of unchanged diamino-acid. The red material was purified by solution in glacial acetic acid and reprecipitation by ether. It was insoluble in water, dilute mineral acids, and most organic solvents, but readily soluble in alkalis, giving neutral solutions (Found: As, 24·8%).

(b) 3 : 4-Diaminophenylarsinic acid, treated in methyl alcohol with ethyl malonate as described by Lewis and Bent (*loc. cit.*), gave the same material, which was purified similarly and dried at 90°. It appears to be malon-*o*-phenyleneamide-4-arsinic acid and, unlike the quinoxalinearsinic acids, gives soluble calcium, barium, and magnesium salts (Found: As, 24·8; N, 9·2. Calc. for $C_9H_9O_5N_2As$: As, 25·0; N, 9·3%).

(3) *Succinic acid*. 3 : 4-Diaminophenylarsinic acid (2 g.), 4*N*-

hydrochloric acid (14 c.c.), and succinic acid (2 g.) gave, on refluxing for 1 hour and cooling, a 60% return of unchanged 3 : 4-diaminophenylarsinic acid. No cyclic arsinic acid could be detected.

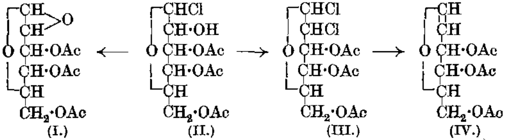
RESEARCH LABORATORIES, MESSRS. MAY & BAKER, LTD., WANDSWORTH, S.W. 18. [Received, October 23rd, 1928.]

CCCCXV.—*Glucosides. Part I. The Formation of Glucosides from 3 : 4 : 6-Triacetyl Glucose 1 : 2-Anhydride.*

By WILFRED JOHN HICKINBOTTOM.

A TRIACETYL glucose anhydride has been prepared by Brigl (*Z. physiol. Chem.*, 1922, **122**, 257), who described it as a crystalline solid which reacted with methyl alcohol to yield a triacetyl β-methylglucoside. This anhydride may therefore prove to be a valuable general reagent for the preparation of glucosides, and more particularly of glucosides which are not obtained conveniently by the usual standard methods. Its reactions with a number of substances have been investigated; those with phenol and with alcohols are here recorded.

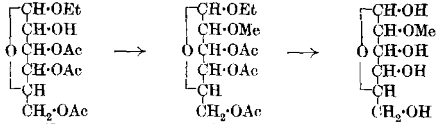
Brigl assigned to the triacetyl glucose anhydride the formula (I) on the basis of its formation from triacetyl glucosyl chloride (II), the structure of which has been determined by its conversion into a triacetyl dichloroglucose (III) and subsequent reduction to triacetyl glucal (IV).



(I.) (II.) (III.) (IV.)

This formulation of the triacetyl glucose anhydride has been confirmed by an independent method. The anhydride was converted, by the interaction of ethyl alcohol and the ethylene oxide group, into 3 : 4 : 6-*triacetyl* β-*ethylglucoside* (V), which, by methylation with methyl iodide in presence of silver oxide, yielded a *triacetyl methyl* β-*ethylglucoside* (VI). Deacetylation by means of alcoholic ammonia, followed by hydrolysis, gave a monomethyl glucose. This sugar was characterised by its *phenylhydrazone*. No phenylosazone could be obtained from it. It must be therefore

2-methyl glucose (VII), as the methyl group can only replace the hydrogen of the remaining hydroxyl group in triacetyl β-ethyl-glucoside.



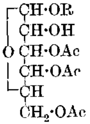
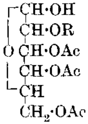
(V.) (VI.) (VII.)

3 : 4 : 6-*Triacetyl glucose anhydride reacts similarly with other* primary and with secondary alcohols at room temperature to yield β-glucosides : methyl alcohol gives a product consisting principally of 3 : 4 : 6-triacetyl β-methylglucoside (compare Brigl, *loc. cit.*), *iso*propyl alcohol furnishes 3 : 4 : 6-triacetyl β-*iso*propylglucoside, and menthol gives 3 : 4 : 6-triacetyl β-menthylglucoside. The last glucoside appears to be identical with the product obtained by Fischer and Bergmann (*Ber.*, 1917, **50**, 711) from the reaction of menthol with tetra-acetyl glucosyl bromide in presence of quinoline. If it is, there must be in Fischer and Bergmann's product a free hydroxyl in position 2. This conclusion is supported by other observations which show that in the tetra-acyl glucosyl halides an acyl group is more readily removed from position 2 than from position 3, 4, or 6. For instance, in 2 : 3 : 4 : 6-tetra-acetyl glucosyl bromide the acetyl group in position 2 is eliminated on reduction to triacetyl glucal. Also 2-trichloroacetyl-3 : 4 : 6-triacetyl glucosyl chloride yields 3 : 4 : 6-triacetyl glucose by combined reduction and regulated hydrolysis (Hickinbottom, unpublished observation) and 3 : 4 : 6-triacetyl glucosyl chloride by carefully controlled deacylation (Brigl, *loc. cit.*).

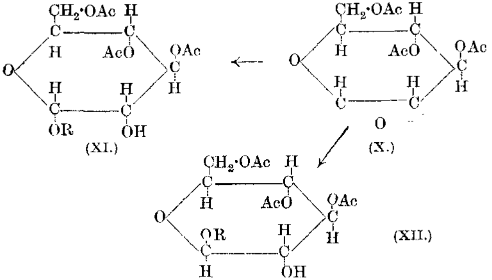
The combination of 3 : 4 : 6-triacetyl glucose anhydride with phenols proceeds less readily than with primary and secondary alcohols. The anhydride and phenol at 80—100° yield a triacetyl phenylglucoside. This was *identified as an* α-*glucoside by conversion* into α-phenylglucoside and into tetra-acetyl α-phenylglucoside and comparison of these substances with authentic specimens. This *method of preparing* α-*phenylglucoside is more convenient than that* described by Fischer and Mechel (*Ber.*, 1916, **49**, 2813), *viz.*, the condensation of phenol with tetra-acetyl glucosyl bromide in the presence of *quinoline*, which yields also a considerable proportion of acetylated β-phenylglucosides.

In all the cases so far examined, the products of the combination of 3 : 4 : 6-triacetyl glucose anhydride (I) with hydroxy-compounds

are glucosides of the type (VIII), no derivative of a 2-alkyl glucose (IX) having yet been isolated.

(VIII.)   (IX.)

To show the relative dispositions of the groups in space, 3 : 4 : 6-triacetyl glucose anhydride may be formulated as in (X).


(XI.) (X.) (XII.)

Then (XI) will represent its α-glucosides, and (XII) the corresponding β-glucosides (compare Drew and Haworth, J., 1926, 2305). It is seen that the formation of β-glucosides by the additive union with alcohols involves the opening of the ethylene oxide ring so that the added groups occupy the *trans*-position. Kuhn and Ebel (*Ber.*, 1925, **58**, 919) also have demonstrated the *trans*-fission of the ethylene oxide ring in *cis*-oxidoethylene-αβ-dicarboxylic acid to yield *r*-tartaric acid. If it be a general behaviour of ethylene oxide rings to yield compounds having *trans*-configurations on fission, it is difficult to explain the formation of 3 : 4 : 6-triacetyl α-phenylglucoside from 3 : 4 : 6-triacetyl glucose anhydride by the action of phenol, unless the α-configuration attributed to the phenylglucoside had been wrongly assigned. The spatial distribution of the glucosidic residue with respect to the rest of the molecule may, however, be deduced from other considerations, *e.g.*, the behaviour towards enzymes, the optical rotatory power, and the formation from glucosyl halides. The evidence from these sources indicates clearly

that the configuration of α-phenylglucoside is not similar to that of β-glucosides.

3 : 4 : 6-Triacetyl glucose anhydride, then, may yield either *cis*- or *trans*-fission products according as it reacts with phenol or alcohols. It appears, therefore, that the configuration of the product resulting from the opening of an ethylene oxide ring cannot be predicted without reference to the nature of the reactants, and probably also to the conditions during the reaction.

α-Glucosan, according to the structure assigned to it by Pictet and Castan (*Helv. Chim. Acta*, 1920, **3**, 645),

$$\overbrace{CH_2(OH)\cdot CH\cdot CH(OH)\cdot CH(OH)\cdot CH\cdot}^{\quad O \quad}\underbrace{CH}_{O},$$

should be the parent substance of 3 : 4 : 6-triacetyl glucose anhydride. The reactions of the two substances differ so widely, however, as to shed doubt on the accuracy of the above structure.

The ethylene oxide ring in α-glucosan is surprisingly stable to reagents in comparison with that in triacetyl glucose anhydride. For instance, α-glucosan may be benzoylated or methylated by means of benzoyl chloride or methyl sulphate in presence of aqueous sodium hydroxide, and it combines additively with methyl iodide in methyl-alcoholic solution at 120° (Cramer and Cox, *Helv. Chim. Acta*, 1922, **5**, 884). Pictet and Castan isolated α-glucosan in a crystalline state by solution in cold methyl alcohol, followed by evaporation at room temperature. Under similar conditions, the ethylene oxide ring in 3 : 4 : 6-triacetyl glucose anhydride, possibly rendered more reactive by the presence of the acyl groups, is opened with the formation of 3 : 4 : 6-triacetyl β-methylglucoside.

The anhydride reacts rapidly with methyl alcohol at room temperature, the formation of the glucoside being complete in about 2 hours for a 5% solution. The rate of reaction with ethyl alcohol is slower, but is sufficiently rapid to prevent the anhydride being purified by crystallisation from this solvent. The graphs in Fig. 1 record the change of optical rotation with time for solutions of 3 : 4 : 6-triacetyl glucose anhydride in methyl and ethyl alcohols.

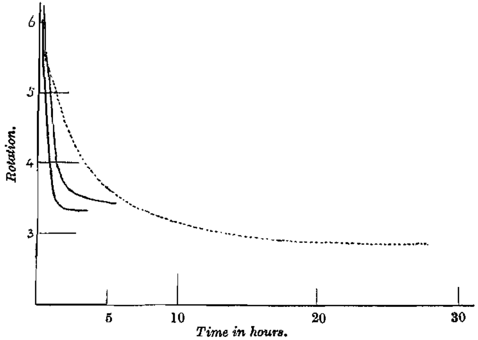
EXPERIMENTAL.

Preparation of 3 : 4 : 6-*Triacetyl Glucose* 1 : 2-*Anhydride* (I) (compare Brigl, *loc. cit.*).—A current of dry ammonia was slowly passed through a suspension of dry, finely powdered 3 : 4 : 6-triacetyl glucosyl chloride in 8—10 times its weight of dry benzene for 3 hours; the mixture was then kept and occasionally shaken in a sealed flask for 15 hours. The ammonium chloride having been removed, and washed with benzene, the filtrate and the washings

were freed from ammonia in a partial vacuum over concentrated sulphuric acid, and the benzene was evaporated under diminished pressure at 40°; addition of light petroleum (b. p. 40—60°) then yielded a crystalline cake of 3 : 4 : 6-triacetyl glucose 1 : 2-anhydride. It separated from a mixture of benzene and light petroleum or from the latter solvent alone in platelets, m. p. 57—58° after sintering at 56°.

The anhydride may also be obtained by shaking with silver oxide a suspension of 3 : 4 : 6-triacetyl glucosyl chloride in dry chloroform for 20 hours. The product, however, is coloured and impure.

FIG. 1.



......*In ethyl alcohol.* ——*In methyl alcohol.*

Reaction of 3 : 4 : 6-*Triacetyl Glucose* 1 : 2-*Anhydride with Hydroxy-compounds.*

With Methyl Alcohol. Formation of 3 : 4 : 6-*Triacetyl* β-*Methyl-glucoside.*—The reaction, which took place readily in the cold, was followed polarimetrically ($l = 2$; $c = 4{\cdot}89$).

t (mins.)	7	15	20	25	30	40	60	120	180
α_D......	+6·11°	5·16°	4·88°	4·60°	4·37°	4·02°	3·67°	3·34°	3·32° (const.)

Similar results were obtained when methyl alcohol containing a trace of methylamine was used as solvent.

Evaporation of the solvent yielded a viscid residue, from which, by crystallisation from absolute alcohol, pure 3 : 4 : 6-triacetyl

β-methylglucoside was obtained in prisms, m. p. 95—97°, $[\alpha]_D$ + 19° (Brigl, *loc. cit.*, gives m. p. 96—98°, $[\alpha]_D$ + 9·4°).

Acetylation in pyridine yielded tetra-acetyl β-methylglucoside which, alone or mixed with a genuine specimen, melted at 101—103°.

With Ethyl Alcohol. Formation of 3 : 4 : 6-*Triacetyl* β-*Ethylglucoside* (V).—A solution of 3 : 4 : 6-triacetyl glucose anhydride in ethyl alcohol deposited on spontaneous evaporation 3 : 4 : 6-*triacetyl* β-*ethylglucoside* in prisms, m. p. 121°, $[\alpha]_D$ + 14·4° in ethyl alcohol (c = 2·57) (Found : C, 50·1; H, 6·7. $C_{14}H_{22}O_9$ requires C, 50·3; H, 6·6%). By slow crystallisation from ethyl alcohol, massive prisms may be obtained having bevelled ends and hexagonal cross-section.

The following rotations were observed for a solution of the anhydride in ethyl alcohol (c = 4·81, l = 2) at 22° :

t (hrs.)	0·13	0·20	0·33	0·55	0·88	1·00	1·67
α_D	+5·90°	5·87°	5·74°	5·57°	5·32°	5·23°	4·75°
t (hrs.)	3·07	3·83	4·85	22·20	26·70		
α_D	4·15°	3·82°	3·63°	2·84°	2·89° (const.)		

The end-point may be reached more rapidly by heating the solution.

The observed constant rotation gives $[\alpha]_D$ + 25·9°, calculated as for triacetyl ethylglucoside. This value is greater than the specific rotation for pure triacetyl β-ethylglucoside in ethyl alcohol. In other experiments also, both with methyl and with ethyl alcohol, the specific rotation of the final solution was greater than that of the pure β-glucoside. It is evident that a small quantity of another substance having a relatively high specific rotation is formed.

Acetylation of the triacetyl β-ethylglucoside with acetic anhydride in pyridine solution gave 2 : 3 : 4 : 6-tetra-acetyl β-ethylglucoside, m. p. 105—106°, which was identified by comparison with a genuine specimen (Found : C, 51·6; H, 6·4. Calc. : C, 51·15; H, 6·6%).

Methylation of 3 : 4 : 6-*triacetyl* β-*ethylglucoside. Formation of* 3 : 4 : 6-*triacetyl*-2-*methyl* β-*ethylglucoside.* Pure triacetyl β-ethylglucoside (0·76 g.) dissolved in an excess of methyl iodide (18 g.) was heated under reflux, with the addition of pure dry silver oxide at intervals during a period of 30 hours. A further 10 g. of methyl iodide was then added, and the heating continued for 10 hours. Dilution with ether, filtration, washing with ether, and evaporation of the filtrate and washings under diminished pressure gave a syrup which rapidly solidified. Crystallisation from ethyl alcohol furnished pure 3 : 4 : 6-*triacetyl*-2-*methyl* β-*ethylglucoside* in needles, m. p. 95—96° (Found : C, 51·9; H, 6·95; OMe + OEt, 21·55. $C_{15}H_{24}O_9$ requires C, 52·05; H, 6·7; OMe + OEt, 21·9%). $[\alpha]_D$ + 5·0° in

ethyl alcohol ($c = 1{\cdot}01$). This glucoside is soluble in benzene, acetone, carbon tetrachloride, and chloroform and moderately easily soluble in cold ethyl alcohol; it is less readily soluble in light petroleum (b. p. 40—60°), from which it crystallises in slender needles.

2-Methyl β-ethylglucoside was obtained as a syrup by removal of the solvent from the product of the action of alcoholic ammonia on triacetyl-2-methyl β-ethylglucoside.

Hydrolysis of 2-methyl β-ethylglucoside with 0·7*N*-hydrochloric acid at 95° for 25 hours, followed by evaporation under diminished pressure after removal of the hydrochloric acid by addition of silver carbonate, gave 2-methyl glucose as a gum containing α- and β-forms. It was characterised by its *phenylhydrazone*, m. p. 175—176° (Found: N, 9·4. $C_{13}H_{20}O_5N_2$ requires N, 9·9%).

2-Methyl glucose was also prepared from β-methyl 3 : 4 : 6-triacetyl glucose by methylation with methyl iodide and silver oxide, followed by deacetylation and hydrolysis. A detailed description of this sugar and its derivatives will be given in a later communication.

With iso*Propyl Alcohol. Formation of* 3 : 4 : 6-*Triacetyl* β-iso-*Propylglucoside*.—Evaporation of a solution of the anhydride in *iso*propyl alcohol which had been kept for several hours gave 3 : 4 : 6-triacetyl β-*iso*propylglucoside. It crystallised only slowly and on acetylation with acetic anhydride in pyridine solution yielded 2 : 3 : 4 : 6-*tetra-acetyl* β-iso*propylglucoside*, which separated from alcohol in needles, m. p. 134—135° (Found: C, 52·3; H, 6·8. $C_{17}H_{26}O_{10}$ requires C, 52·3; H, 6·7%). $[\alpha]_D$ − 23·4° in alcohol. The tetra-acetyl glucoside is sparingly soluble in water and only moderately easily soluble in cold ethyl alcohol.

With Benzyl Alcohol. Formation of 3 : 4 : 6-*Triacetyl* β-*Benzylglucoside*.—3 : 4 : 6-Triacetyl glucose 1 : 2-anhydride was heated at 100° with benzyl alcohol. After 2 hours, the excess of alcohol was removed under diminished pressure at 100°. The residual 3 : 4 : 6-triacetyl benzylglucoside, after being washed with light petroleum, was converted into β-benzylglucoside, m. p. 119°, $[\alpha]_D$ − 49°, by the action of alcoholic ammonia.

Acetylation of the benzylglucoside yielded 2 : 3 : 4 : 6-tetra-acetyl β-benzylglucoside, m. p. 98—99°, $[\alpha]_D$ − 44° in alcohol (Found: C, 57·5; H, 6·0. Calc.: C, 57·7; H, 6·0%). Fischer and Helferich (*Annalen*, 1911, **383**, 68) give m. p. 96—101° (corr.), $[\alpha]_D$ − 48°.

With Menthol. Formation of 3 : 4 : 6-*Triacetyl* β-*Menthylglucoside*.—The anhydro-compound was heated with an equal weight of benzene and three times its weight of menthol at 90—100° for 30 hours. The excess of menthol was removed under diminished pressure at 100°, leaving a residue of 3 : 4 : 6-triacetyl menthylglucoside. A

filtered solution in ether, on treatment with light petroleum, gave triacetyl menthylglucoside, which was crystallised from carbon tetrachloride or alcohol; m. p. 144° after sintering at 141°, $[\alpha]_D$ − 10·6° in benzene. β-Menthylglucoside was obtained conveniently from the triacetyl glucoside by the action of aqueous-alcoholic potassium hydroxide. Fischer and Bergmann (*Ber.*, 1917, **50**, 711) describe a triacetyl β-menthylglucoside having m. p. 143—146°, and $[\alpha]_D$ − 12·6° in benzene.

With Phenol. Formation of 3 : 4 : 6-*Triacetyl* α-*Phenylglucoside*.—As phenol and the anhydro-compound in benzene reacted only slowly at room temperature, a mixture of phenol with approximately one-third of its weight of 3 : 4 : 6-triacetyl glucose anhydride was maintained at 100° for about 20 hours. After removal of unused phenol at 100° under diminished pressure, the residue of triacetyl phenylglucoside was acetylated in pyridine solution. Crude 2 : 3 : 4 : 6-tetra-acetyl α-phenylglucoside, m. p. 109—110°, resulted, and by one crystallisation from alcohol, the melting point was raised to 112°. This value was not altered by further recrystallisation or by admixture with a genuine specimen of tetra-acetyl α-phenylglucoside. $[\alpha]_D$ + 162° in alcohol (c = 1·0). Fischer and Mechel (*loc. cit.*) give m. p. 115° (corr.), $[\alpha]_D$ + 164·9° in benzene.

A solution of tetra-acetyl phenylglucoside in twenty times its weight of dry alcohol was saturated with dry ammonia at room temperature and then kept for 15 hours. After removal of the alcohol at 30° in a partial vacuum, and thorough washing with dry ether to remove acetamide, the residue solidified, m. p. 168—169°. Crystallisation from ethyl acetate gave *α-phenylglucoside hydrate*, m. p. 155—160°, $[\alpha]_D$ + 157° in alcohol (Found: C, 52·8; H, 6·7. $C_{12}H_{16}O_6,H_2O$ requires C, 52·5; H, 6·6%).

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EDGBASTON. [*Received, October 6th*, 1928.]

CCCCXVI.—*The Structure of the Normal Monosaccharides. Part V. Lyxose.*

By EDMUND LANGLEY HIRST and JAMES ANDREW BUCHAN SMITH.

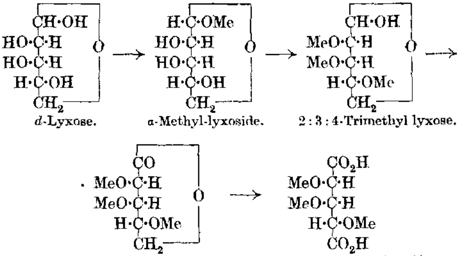
IT has been shown (J., 1923, **123**, 1352 and subsequent papers) that when the normal trimethyl derivatives of xylose, arabinose, and rhamnose are oxidised by nitric acid the reaction leads in each case

to the formation of a trimethoxyglutaric acid. This implies that in each of these three trimethyl pentoses the methoxyl groups are attached to the second, third, and fourth carbon atoms, and that the oxygen of the ring must he attached to the fifth carbon atom. The normal trimethyl pentoses are known to possess the same oxide ring structure as the corresponding normal methylpentosides, and it follows, therefore, that the normal forms of methylxyloside, methylarabinoside, and methylrhamnoside contain the amylene-oxide ring and belong to the pyranose group of sugar compounds.

Similar experimental methods have been now applied to determine the structure of α-methyl-lyxoside and definite proof has been obtained that this substance and its derivatives are of the pyranose type and thus conform to the general rule followed by normal sugar derivatives. Moreover, in view of the optical relationships which exist between the α-form of lyxose and α-methyl-lyxoside (Phelps and Hudson, *J. Amer. Chem. Soc.*, 1926, **48**, 503), this variety at least of the free sugar may be presumed to possess the pyranose structure. An examination of the structural relationships which exist between the α- and β-modifications of lyxose has been contributed in an earlier paper (Haworth and Hirst, this vol., p. 1221).

The normal trimethyl lyxose required for the oxidation experiments was prepared by methylating crystalline α-methyl-lyxoside with Purdie's reagents. This method of preparation ensures the formation of a *trimethyl methyl-lyxoside*, retaining the oxide ring structure of the original α-methyl-lyxoside. Other experiments showed that the same pyranose form of trimethyl methyl-lyxoside was produced by the direct methylation of lyxose with methyl sulphate. Hydrolysis of the trimethyl methyl-lyxoside gave crystalline *trimethyl lyxose*, m. p. 79°. The constitution of this substance as 2 : 3 : 4-trimethyl lyxose followed at once from a study of its oxidation by nitric acid, and also from the nature of the *trimethyl-lyxonolactone* obtained from it by the action of bromine water. The lactone, which was characterised by the preparation of the corresponding crystalline *phenylhydrazide*, m. p. 180—181°, displayed the behaviour typical of a δ-lactone. Polarimetric observations during its hydrolysis in aqueous solution showed that equilibrium was attained in about 60 hours, and that some 9% of the lactone then remained unchanged. When oxidised with nitric acid the lactone gave exclusively *d*-trimethoxyglutaric acid, which was identified both as the crystalline amide, the enantiomorph of which was originally prepared from *l*-arabinose (Hirst and Robertson, J., 1925, **127**, 358), and as the methylamide (Goodyear

and Haworth, J., 1927, 3145; see also Haworth and Jones, *ibid.*, p. 2349).



d-Lyxose. α-Methyl-lyxoside. 2 : 3 : 4-Trimethyl lyxose.

Trimethyl-δ-lyxonolactone. *d*-Trimethoxyglutaric acid.

These results were in themselves sufficient to warrant the allocation of the pyranose structure to α-methyl-lyxoside, but in order to render the evidence as strong as possible, experiments were made to determine the effect of nitric acid on trimethyl methyl-lyxoside. The product of the reaction was again *d*-trimethoxyglutaric acid, the pure distilled methyl ester of which was obtained in yields corresponding to 80% of the theoretical. From the ester 88% of the theoretical quantity of pure crystalline *d*-trimethoxyglutaramide was isolated. Since the methylation of methyl-lyxoside proceeded almost quantitatively, it follows that by this method, in spite of the lengthy series of operations involved, some 70% of the calculated quantity of *d*-trimethoxyglutaramide can be obtained from methyl-lyxoside. Control experiments have shown that, under the experimental conditions adopted, nitric acid is without appreciable effect on the products of oxidation, and no product other than trimethoxyglutaric acid could be detected in the present case. In none of the numerous investigations in which this mode of oxidation has been employed has there been any sign of the migration of methoxy-groups under the influence of nitric acid, and the results obtained are both mutually consistent and in agreement with the evidence furnished by independent chemical methods of examination.

Emphasis is laid on the foregoing considerations in view of the total disagreement which exists between the conclusions now drawn from the chemical evidence and the views of Phelps and Hudson (*loc. cit.*), who assign to α-methyl-lyxoside and its derivatives a butylene-oxide formula. These authors have compared the mole-

cular rotations of the two pairs of epimeric substances α-methyl-lyxoside and α-methylxyloside, and α-methylmannoside and α-methylglucoside. They find between each pair a difference in $[M]_D$ of about 15,500 units, which is taken to indicate the existence of similar structural relationships between the members of each pair, a conclusion with which the experimental results now presented are in complete agreement. Since, however, they regard α-methylxyloside and α-methylmannoside as 1 : 5-oxides and α-methylglucoside as a 1 : 4-oxide, it is argued that α-methyl-lyxoside must be similar in structure to α-methylglucoside and therefore a 1 : 4-oxide. In a later paper (*J. Amer. Chem. Soc.*, 1928, **50**, 2049) they reach similar conclusions from a study of the rotations of the acetylated derivatives of these four methyl-glycosides, the α-methylglucoside used for comparison being now the hypothetical 1 : 5-compound whose rotation has been calculated by Hudson. It is obvious that the validity of this mode of reasoning is dependent on the certainty with which the furanose structure can be assigned to α-methylglucoside and the pyranose structure to its hypothetical isomeride. It will be remembered that as a basis for the argument used in demonstrating the presence of a 1 : 4-ring in α-methylglucoside Hudson (*J. Amer. Chem. Soc.*, 1926, **48**, 1424, 1434) accepted the pyranose structure of α-methylxyloside and of α-methylarabinoside on the ground that it had been established experimentally by oxidation methods. It is evident, therefore, that experiments of a precisely similar nature carried out with α-methyl-lyxoside would provide a critical test of the accuracy of the optical method in assigning ring structures. These experiments have now been performed, and the results permit of no reasonable interpretation other than that α-methyl-lyxoside possesses a pyranose structure. A furanose structure was, however, deduced from the optical data and an obvious inconsistency is thus made manifest, which can be removed most simply by accepting the chemical evidence for the pyranose structure of α-methylglucoside. If this be done, the optical relationships existing between the four methylglycosides considered by Phelps and Hudson then agree with the chemical evidence in supporting the pyranose structure of all these compounds. It thus follows that the observations now recorded lend additional support to the reasons which have already been advanced (Drew and Haworth, J., 1926, 2303; Haworth and Hirst, *loc. cit.*) for doubting the validity of certain assumptions made by Hudson in deducing the furanose structure of α-methylglucoside.

EXPERIMENTAL.

Trimethyl Methyl-lyxoside.—Crystalline methyl-lyxoside (m. p. 109°) (7·2 g.) was dissolved in methyl iodide (20 c.c.) and treated

with silver oxide (35 g.) in the usual manner. After the fourth successive methylation under these conditions the product was distilled, giving *trimethyl methyl-lyxoside* as a colourless mobile oil (8·7 g.), b. p. about 70°/0·02 mm., $n_D^{14°}$ 1·4460, $[\alpha]_{5461}^{20°}$ + 10° in water (c = 2·61), $[\alpha]_{5461}^{20°}$ + 37·3° in alcohol (c = 4·05). The substance, which possessed typical glucosidic properties, resisted all attempts to crystallise it. The absence of oxidation products in the form of lactones or esters was proved by heating a weighed portion (0·196 g.) for 30 minutes with 5 c.c. of N/10-sodium hydroxide, 5 c.c. of N/10-sulphuric acid being then required to titrate the remaining alkali. The mode of preparation and its specific rotation indicated that the trimethyl methyl-lyxoside consisted largely of the α-isomeride (Found: C, 51·8; H, 8·7; OMe, 58·8. $C_9H_{18}O_5$ requires C, 52·4; H, 8·7; OMe, 60·2%).

Trimethyl Lyxose.—Trimethyl methyl-lyxoside (4·0 g.) was hydrolysed by heating it at 100° with 6% aqueous hydrochloric acid (120 c.c.). In the course of one hour the specific rotation altered from $[\alpha]_{5461}^{20°}$ + 7° to a constant value $[\alpha]_{5461}^{20°}$ − 19°. The hydrochloric acid was then neutralised with barium carbonate and the *trimethyl lyxose* was extracted from the solution by chloroform. The product (3·6 g.) was distilled, giving a mobile, colourless liquid, (3·3 g.), b.p. 90°/0·05 mm., $n_D^{15°}$ 1·4629. After being kept for 12 hours, the distillate became viscid and finally set to a solid glass, which crystallised when rubbed. In subsequent experiments the distillation was omitted and the trimethyl lyxose crystallised when nucleated (yield, 85%). Recrystallisation from light petroleum gave trimethyl lyxose in long needles, m. p. 79°, $[\alpha]_D^{20°}$ − 22° in water (equilibrium value; c = 2·01) (Found: C, 50·0; H, 8·4; OMe, 48·2. $C_8H_{16}O_5$ requires C, 50·0; H, 8·3; OMe, 48·4%).

The mutarotation of normal trimethyl lyxose was rapid in aqueous solution, the equilibrium value being reached in less than 30 minutes at 21°. The following table gives the details of a typical experiment (c = 2·01).

Time (mins.)	1·5	3·3	4·3	6·0	7·8	10·0
$[\alpha]_D^{21°}$	−11·9°	13·4°	14·4°	14·9°	15·9°	17·4°
Time (mins.)	11·8	15	20	28	250	
$[\alpha]_D^{21°}$	17·8°	19·4°	21°	21·8°	21·8°	

From these figures the initial rotation was calculated to be $[\alpha]_D^{21}$ − 10°, and the mean value for $k_1 + k_2$ was found to be 0·045 (*t* in mins.). Observations were made of the specific rotation in methyl alcohol containing 1% of hydrogen chloride before and after heating the solution. The values were respectively $[\alpha]_D^{20°}$ − 7·1° (c = 0·77) and $[\alpha]_D^{20°}$ + 21° (c = 0·83). In the latter case the concentration is that of the trimethyl methyl-lyxoside formed during the reaction

and the observation gives the specific rotation of the equilibrium mixture of the α- and β-isomerides of normal trimethyl methyl-lyxoside.

Methylation of Lyxose with Methyl Sulphate.—Lyxose (10 g.), dissolved in the least possible amount of water, was treated with methyl sulphate (76 c.c.) and 50% aqueous sodium hydroxide solution (140 c.c.), the usual precautions being taken. The product (12 g.) was then subjected to two successive methylations with methyl iodide and silver oxide. On distillation, trimethyl methyl-lyxoside was obtained as a colourless oil (10·6 g.), b. p. about 70°/0·02 mm., $n_D^{14°}$ 1·4471, $[\alpha]_D^{20°}$ − 6° in methyl alcohol (c = 1·44). After being heated with methyl alcohol containing 1% of hydrogen chloride, the trimethyl methyl-lyxoside gave as the equilibrium value $[\alpha]_D^{20°}$ + 20·6°. The trimethyl methyl-lyxoside prepared in this manner therefore contained excess of the β-isomeride, and gave the same equilibrium value for the specific rotation as normal trimethyl methyl-lyxoside (Found: OMe, 58·8. Calc.: OMe, 60·2%). Further evidence confirming the absence of the furanose isomeride was obtained in the following way. During hydrolysis with 6% aqueous hydrochloric acid, the rotation of the solution changed to $[\alpha]_D^{20°}$ − 22° (calculated as trimethyl lyxose), which is very near to the value recorded for normal trimethyl lyxose, and the yield of crystalline trimethyl lyxose, m. p. 79°, isolated after hydrolysis was 90% of the theoretical.

Trimethyl-lyxonolactone.—A solution of trimethyl lyxose (9 g.) in water (60 c.c.) was treated with bromine (8—10 c.c.), the bromine being added gradually and the temperature maintained at 35° until the reducing properties of the solution had disappeared. This required several days, after which the excess of bromine was removed by aëration. The solution was then neutralised with silver oxide and filtered and the dissolved silver was removed as silver chloride by addition of the exact quantity of hydrochloric acid, the end-point being determined with the aid of Congo-paper. The water was then removed under diminished pressure. The residual syrup was heated at 100°/12 mm. for some hours to complete lactonisation and was then distilled, giving *trimethyl-δ-lyxonolactone* as a liquid, b. p. 105°/0·02 mm., $n_D^{18°}$ 1·4620 (yield, 8·0 g.). $[\alpha]_D^{19°}$ + 35·5° (initial value); $[\alpha]_D^{19°}$ − 9·3° (equilibrium value), both in water (c = 1·2) (Found: C, 50·3; H, 7·4; OMe, 49·1. $C_8H_{14}O_5$ requires C, 50·5; H, 7·4; OMe, 48·9%). 0·1232 G. of the
δ- substance required 7·0 c.c. of N/10-sodium hydroxide for neutralisation (calc., 6·9 c.c.).

*Tri*The lactone, although analytically pure, could not be made to
109°) (7·2 lise. When, however, it was heated on the water-bath with

the exact quantity of phenylhydrazine dissolved in a little ether, it readily formed the crystalline phenylhydrazide of the corresponding acid. The solid product (yield 80%), after being washed with ether, was found to be the pure *phenylhydrazide* of 2 : 3 : 4-trimethyl-lyxonic acid, m. p. 180—181°, remaining unaltered after two recrystallisations from benzene (Found: C, 56·5; H, 7·7; N, 9·6; OMe, 30·9. $C_{14}H_{22}O_5N_2$ requires C, 56·3; H, 7·4; N, 9·4; OMe, 31·2%).

Attempts to obtain the lactone in a crystalline condition by regenerating it from the crystalline phenylhydrazide yielded material identical with that described above.

Hydrolysis of the lactone. The velocity of hydrolysis in aqueous solution was determined by polarimetric observation, the mean value for $k_1 + k_2$ being 0·027 at 19° (*t* in hours). Equilibrium was reached in about 3 days at 19°. The rotation of the corresponding acid was obtained in the following manner. A weighed amount of the lactone was dissolved in excess of standard sodium hydroxide solution. The exact amount of sulphuric acid equivalent to the alkali was added, and the rotation was observed immediately; $[\alpha]_D^{19°}$ — 13·4° (calc. as lactone). The proportion of lactone present at equilibrium was therefore 9·1%.

t (hrs.).	$[\alpha]_D^{19°}$.	% Lactone.	*t* (hrs.).	$[\alpha]_D^{19°}$.	% Lactone.
0	+35·5°	100	51·5	—7·7°	12·4
18·0	5·1	38·3	66·5	9·3	9·1
27·8	— 0·8	26·4	90·5	9·3	9·1
42·5	6·1	15·6	200	9·3	9·1

Oxidation of Trimethyl-lyxonolactone.—A solution of the lactone (1·6 g.) in nitric acid (*d* 1·42; 25 c.c.) was heated gently on the water-bath until the vigorous reaction had ended, and then for 1½ hours at 90°. The nitric acid was removed by distillation under diminished pressure, and the syrupy residue boiled for 5 hours with 3% methyl-alcoholic hydrogen chloride (25 c.c.). The solution, after being neutralised with silver oxide, was evaporated to a syrup, which gave on distillation methyl trimethoxyglutarate (1·6 g., or 76% of the theoretical), b. p. about 100°/0·1 mm., $n_D^{21°}$ 1·4353, $[\alpha]_D^{20°}$ — 39° in methyl alcohol (c = 0·4), $[\alpha]_D^{20°}$ — 31° in water (c = 1·51) (Found: OMe, 59·0; CO_2Me, by titration, 46·2. Calc.: OMe, 62·0; CO_2Me, 47·2%). Treatment of the ester with methyl-alcoholic ammonia gave trimethoxyglntaramide, m. p. 230° (decomp.), $[\alpha]_D^{20°}$ — 49° in water (c = 0·7). Methyl-alcoholic methylamine gave similarly the methylamide, m. p. 171—172° alone or when mixed with a specimen of the methylamide of the trimethoxyglutaric acid obtainable from tetramethyl-δ-mannonolactone (Goodyear and Haworth, *loc. cit.*). The high yields of pure

amide and methylamide (in each case, more than 70% of the theoretical) served to prove the homogeneity of the liquid ester.

Additional oxidation experiments were performed in order to determine the largest possible yields of crystalline trimethoxyglutaramide obtainable from α-methyl-lyxoside. For this purpose trimethyl methyl-lyxoside (prepared as above from α-methyl-lyxoside) was heated with nitric acid (*d* 1·42) under conditions exactly similar to those given above for the oxidation of the trimethyl-lyxonolactone. In this way 1·6 g. of trimethyl methyl-lyxoside gave 1·7 g. of distilled methyl trimethoxyglutarate, $n_D^{20°}$ 1·4355, $[\alpha]_D^{20°}$ − 34° in water (c = 1·3).

The values now recorded of $[\alpha]_D^{20°}$ for methyl trimethoxyglutarate are regarded as more nearly correct than those given in earlier papers (compare Hirst and Robertson, *loc. cit.*; McOwan, J., 1926, 1747). Dilute nitric acid was used in the previous work and it is probable that the ester then obtained contained a little trimethyl-δ-arabonolactone, *insufficient in amount to affect the analyses but* sufficient, owing to the exceedingly large rotation of the lactone, to affect the observed rotation value. That no racemisation or structural change has occurred in the present experiment is proved by the fact that nearly theoretical yields (88%) of the crystalline amide, m. p. 230° (decomp.), were obtained when the ester was treated with methyl-alcoholic ammonia. The specific rotation of this amide, $[\alpha]_D^{20°}$ − 49° in water (c = 0·9), agreed exactly with the observations previously recorded. The overall yield of amide from α-methyl-lyxoside was therefore 70%. The corresponding methylamide, m. p. 171—172°, was also prepared from the ester (yield 80%).

The authors wish to thank Professor W. N. Haworth, D.Sc., F.R.S., for his interest in this work, and one of them (J. A. B. S.) desires to express his gratitude to the Department of Scientific and Industrial Research for the award of a maintenance grant, and to the Chemical Society for a grant which has in part defrayed the cost of the experiments.

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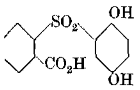
EDGBASTON. [*Received, October 19th, 1928.*]

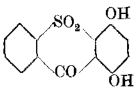
CCCCXVII.—*Hydroxy-derivatives of Thioxanthone Dioxide.*

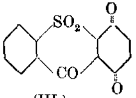
By WILLIAM BENNETT PRICE and SAMUEL SMILES.

DURING an examination of the abnormal properties of 1-methoxy- and 1-hydroxy-thioxanthones a comparison with the corresponding sulphones was desirable. The only method hitherto used for the

preparation of substituted thioxanthone dioxides is the oxidation of the corresponding thioxanthone with hydrogen peroxide or similar agents (Ullmann and Glenck, *Ber.*, 1916, **49**, 2491). This process is generally valuable, but the application to hydroxythioxanthones is not always successful, particularly in the case of 1 : 4-dihydroxy-derivatives. An effective process leading to the 1 : 4-dihydroxythioxanthone dioxide and certain of its derivatives has been found in the action of 2-sulphinobenzoic acid upon *p*-benzoquinones. In accordance with the general behaviour of sulphinic acids with quinones (Hinsberg, *Ber.*, 1894, **27**, 3259) 2 : 5-*dihydroxydiphenylsulphone-2'-carboxylic acid* (I) was obtained which by dehydration yielded the thioxanthone dioxide (II).


(I.)


(II.)


(III.)

The interesting quinone (III) was isolated when this 1 : 4-dihydroxy-derivative was oxidised with lead tetra-acetate. The union of 2-sulphinobenzoic acid with simple *p*-quinones such as toluquinone and chlorobenzoquinone took place easily and even with quinizarinquinone the substituted phenylanthraquinonylsulphone (IV) was obtained, but in this case dehydration yielding the thioxanthone dioxide could not be effected. Union of 1 : 2-naphthaquinone and this sulphinic acid did not take place in the normal manner, but gave an unstable additive product containing an additional molecule of water. Dehydration of this material by heating it alone or in solvents removed water (2 mols.) and gave a product which is to be regarded as the sulphoxide (V) derived from 1 : 2-naphthaquinone, since it yielded a phenylhydrazone and a phenazine and on being heated with acetic anhydride gave the naphthathioxanthonequinone (VI).

$$C_6H_4{<}{}^{CO}_{CO}{>}C_6H(OH)_2{<}{}^{SO_2}_{HO_2C}{>}C_6H_4 \quad (IV.) \qquad C_{10}H_5(:O)_2{\cdot}SO{\cdot}C_6H_4{\cdot}CO_2H \quad (V.)$$

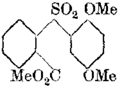
$$C_6H_4{<}{}^{S-}_{CO}{>}C_{10}H_4(:O)_2 \qquad (VI.)$$

The 2-thiobenzoic group could be easily removed from this primary additive product by reduction, whereas this group in the sulphoxide quinone (V) was relatively stable to mild reducing agents. For these reasons it is suggested that the primary product of reaction between 1 : 2-naphthaquinone and 2-sulphinobenzoic acid is best represented by the structure (VII), the sulphinic acid reacting in the

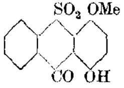
tautomeric hydroxy-form R·SO·OH. This case is evidently similar to that encountered by Hinsberg (*Ber.*, 1919, **52**, 28) in the union of 1 : 4-naphthaquinone with naphthalene-1-sulphinic acid. Hinsberg isolated from these reagents an additive product which under the action of heat lost water and was converted into the sulphoxide (compare V) derived from 1 : 4-naphthaquinone. It was thought that this abnormal behaviour of naphthalene-1-sulphinic acid and of 2-sulphinobenzoic acid might be associated with the ortho-substituent contained by them, but preliminary experiments with other ortho-substituted sulphinic acids and 1 : 2-naphthaquinone have given the usual type of sulphone. Further investigation of the necessary conditions is being made.

$O{:}C_{10}H_6{<}^{OH}_{O\cdot SO\cdot R}$

(VII.)



(VIII.)



(IX.)

In a study of the methylation of these hydroxythioxanthor dioxides in alkaline media the usual inhibitory effect of the orth carbonyl group was observed in the 1-hydroxy-derivatives. F instance, the 2-*methoxy*- and 2 : 3-*dimethoxy-thioxanthone dioxid* were easily obtained from the hydroxy-compounds by this metho but the 1 : 4-dihydroxy-derivative (II) was only slightly attack even under intense conditions, the chief product being then 1-*hydrox* 4-*methoxythioxanthone dioxide* (IX). The ortho-sulphonyl gro does not exert this inhibitory effect in alkaline methylation. F example, *p*-cresol-*o*-sulphone was rapidly alkylated and 2 : 5-hydroxydiphenylsulphone-2′-carboxylic acid (I) gave alm theoretical yields of the *ester* (VIII). Similar results were obtair with other hydroxy-sulphones.

EXPERIMENTAL.

When equimolecular quantities of 2-sulphinobenzoic acid a *p*-benzoquinone or its simple derivatives were shaken with wa (100 c.c. : 2 g. of reagents) reaction was complete in 1—2 hours. small quantity of tarry material was usually formed; this removed and the desired product, which separated from liquid, was collected. The following are examples of hydr derivatives of diphenylsulphone obtained by this method. 2 : 5 *hydroxydiphenylsulphone-2′-carboxylic acid* (I), from *p*-benzoquir and 2-sulphinobenzoic acid, formed prisms, m. p. 235° (Fou C, 53·0; H, 3·6; S, 10·8. $C_{13}H_{10}O_6S$ requires C, 53·0; H, S, 10·8%). The *diacetyl* derivative, needles from acetic acid,

m. p. 188° (Found: C, 53·9; H, 3·8. $C_{17}H_{14}O_8S$ requires C, 53·9; H, 3·7%). When methyl sulphate (5 mols.) was added to a hot solution of this dihydroxy-acid (1 mol.) in aqueous sodium hydroxide (6 mols.) an almost theoretical yield of *methyl 2 : 5-dimethoxydiphenylsulphone-2'-carboxylate* (VIII), m. p. 195°, separated (Found: C, 57·1; H, 4·7. $C_{16}H_{16}O_6S$ requires C, 57·1; H, 4·7%). Hydrolysis of this ester yielded 2 : 5-*dimethoxydiphenylsulphone-2'-carboxylic acid*, which separated in plates, m. p. 223°, from acetic acid (Found: C, 55·7; H, 4·2. $C_{15}H_{14}O_6S$ requires C, 55·9; H, 4·3%).

Methyl-2 : 5-dihydroxydiphenylsulphone-2'-carboxylic acid, from 2-sulphinobenzoic acid and *p*-toluquinone, formed needles, m. p. 203° (Found: C, 54·4; H, 3·8. $C_{14}H_{12}O_6S$ requires C, 54·5; H, 3·9%).

Chloro-2 : 5-dihydroxydiphenylsulphone-2'-carboxylic acid, from chlorobenzoquinone and the sulphinic acid, separated from acetic acid in fine needles, m. p. 210° (Fonnd: C, 47·4; H, 2·8. $C_{13}H_9O_6ClS$ requires C, 47·4; H, 2·7%). Sulphones of this type which form an intermediate stage in the synthesis of thioxanthone dioxides may also be obtained by oxidation of the corresponding sulphides, these being available from the reaction of phenols with the dichloride of 2-sulphinobenzoic acid (this vol., p. 2859). In certain cases this alternative may not be availahle. For example, when 2 : 4-dihydroxy-2'-carboxydiphenyl sulphide (this vol., p. 2862) was treated in the usual manner with hydrogen peroxide or similar agents the required sulphone could not be isolated, and restricted action of hydrogen peroxide led to 2 : 4-*dihydroxy-2'-carboxydiphenyl sulphoxide*, $C_6H_3(OH)_2{\cdot}SO{\cdot}C_6H_4{\cdot}CO_2H$, which gave a purple solution with sulphuric acid and had m. p. 204° (Found: C, 56·3; H, 3·7. $C_{13}H_{10}O_5S$ requires C, 56·1; H, 3·6%). This did not yield the corresponding thioxanthone with the usual dehydrating agents.

2-*Quinizarinphenylsulphone-2'-carboxylic Acid* (IV).—Acetic acid (20 c.c.; 1 g. of reagents) containing equal weights of quinizarinquinone and the sulphinic acid was boiled until separation of the products began. The *sulphone* was collected from the cooled liquid and purified from nitrobenzene; it formed red needles, m. p. 263°, and gave a blne solution in aqueous alkali hydroxide (Found: C, 59·2; H, 2·9. $C_{21}H_{12}O_8S$ requires C, 59·4; H, 2·8%).

Derivatives of Thioxanthone Dioxide.—Condensation of the 2-carboxy-derivatives of diphenylsulphone was effected by heating (100°) the solutions in sulphuric acid for varying periods, the progress of the reaction being indicated by the development of the intense red colour due to the thioxanthone dioxide. The products were isolated after addition of ice.

1 : 4-*Dihydroxythioxanthone dioxide* (II) separated from acetic acid in orange needles, m. p. 224°, which gave a crimson solution in

aqueous alkali (Found: C, 56·2; H, 3·0. $C_{13}H_8O_5S$ require C, 56·5; H, 2·9%). The *diacetyl* derivative separated from alcohc in yellow needles, m. p. 174° (Found: C, 56·7; H, 3·3. $C_{17}H_{12}O_7$ requires C, 56·6; H, 3·3%).

Methyl-1 : 4-*dihydroxythioxanthone dioxide* formed orange plates m. p. 175°, from acetic acid (Found: C, 57·5; H, 3·7. $C_{14}H_{10}O_5$ requires C, 57·9; H, 3·4%).

Chloro-1 : 4-*dihydroxythioxanthone dioxide* was obtained in simila form, m. p. 230° (Found: C, 50·3; H, 2·5. $C_{13}H_7O_5ClS$ require C, 50·2; H, 2·2%).

Thioxanthone Dioxide 1 : 4-*Quinone* (III).—A thin paste of th 1 : 4-dihydroxy-derivative (2 g.) and acetic acid was triturated wit lead tetra-acetate (4 g.). After 4 days the solid was collected an purified from benzene. The desired product was thus obtained i yellow needles, m. p. 185°, which liberated iodine from aqueou potassium iodide (Found: C, 56·7; H, 2·2. $C_{13}H_6O_5S$ require C, 56·9; H, 2·2%).

1 : 4-*Dimethoxythioxanthone dioxide* was obtained either by oxid ation of 1 : 4-dimethoxythioxanthone (Clarke and Smiles, J., 1911 **99,** 1535) with hydrogen peroxide in warm acetic acid or by heatin 2 : 5-dimethoxydiphenylsulphone-2′-carboxylic acid or its methy ester with sulphuric acid. The substance separated from aceti acid in pale yellow needles, m. p. 193° (Found: C, 59·1; H, 4·1 $C_{15}H_{12}O_5S$ requires C, 59·2; H, 3·9%). It is also formed when th dihydroxy-compound is submitted to alkaline methylation, but th yields are poor even under intense conditions. The followin experiment is quoted in illustration. The dark red potassium sal of the dihydroxythioxanthone dioxide was heated (130°) for 6 hour with excess of methyl sulphate. After the mixture had been cooled the excess of the ester was decomposed by aqueous alkali. Th dimethyl ether was then obtained (7—8%) from the materia unattacked by alkali hydroxide, and from the remainder th 1-hydroxy-4-methoxy-derivative (IX) was isolated by means of th sparingly soluble sodium salt. This monomethyl ether (m. p. 184° was identified with a sample prepared by another synthesis which wi be described in a future communication.

2-*Hydroxythioxanthone Dioxide*.—When phenol and 2-thiolbenzoi acid were dissolved in warm sulphuric acid (Christopher and Smile J., 1911, **99**, 2050), or when the product from phenol and th dichloride of 2-sulphinobenzoic acid (this vol., p. 2862) was treate with this solvent, a hydroxythioxanthone was formed which o methylation yielded a methoxythioxanthone identical with th 2-derivative. The constitution of the latter was determined by synthesis which will be subsequently described.

A solution of this 2-hydroxythioxanthone and excess of hydrogen peroxide in hot acetic acid was kept at 100° during 1 hour. The required *sulphone* then separated in shining yellow needles, m. p. 259° (Found: C, 59·7; H, 3·2. $C_{13}H_8O_4S$ requires C, 60·0; H, 3·0%). 2-*Methoxythioxanthone dioxide*, m. p. 204°, was obtained in good yield by alkaline methylation and formed pale yellow plates from acetic acid (Found: C, 61·0; H, 3·6. $C_{14}H_{10}O_4S$ requires C, 61·3; H, 3·6%).

2 : 3-*Dihydroxythioxanthone Dioxide.*—When pyrocatechol was submitted to the same treatments as phenol in the foregoing case, a dihydroxythioxanthone was obtained. It was identical with a sample of the 2 : 3-derivative prepared by another synthesis. When this substance was oxidised in the usual manner the required *sulphone* was obtained in yellow needles, m. p. 203° (decomp.) (Found: C, 56·2; H, 3·1. $C_{13}H_8O_5S$ requires C, 56·5; H, 2·9%). Aqueous alkaline methylation of this material gave good yields of 2 : 3-*dimethoxythioxanthone dioxide*, which formed long, yellow needles, m. p. 241°, from acetone (Found: C, 59·2; H, 4·2. $C_{15}H_{12}O_5S$ requires C, 59·2; H, 3·9%).

Naphthalene Derivatives.—An aqueous solution (400 c.c.) of 2-sulphinobenzoic acid (3·6 g.) was added to a stirred suspension of 1 : 2-naphthaquinone (2·4 g.) in water (50 c.c.). When the quinone had disappeared, the tarry matter was removed from the clear solution, the latter kept for 2 days, and the crystalline product purified from alcohol–water.

The desired *additive product* (VII) was thus obtained in shining plates, m. p. 156° (decomp.), which were sparingly soluble in water and readily soluble in alcohol (Found: C, 56·2; H, 4·2; S, 8·7. $C_{17}H_{12}O_6S,H_2O$ requires C, 56·3; H, 3·9; S, 8·8%). When a solution of this material in 10 times its weight of acetic acid was boiled for 1 hour, 1 : 2-*naphthaquinone* 2′-*carboxyphenyl sulphoxide* (V) was obtained. This separated from the cooled liquid in red needles, m. p. 236°, which were sparingly soluble in most organic media (Found: C, 62·2; H, 3·3; S, 9·8. $C_{17}H_{10}O_5S$ requires C, 62·6; H, 3·0; S, 9·8%). This quinone yielded, after reaction with phenylhydrazine in acetic acid, a *phenylhydrazone*, m. p. 251° (Found: N, 6·7. $C_{23}H_{16}O_4N_2S$ requires N, 6·7%). Also the *quinoxaline* derivative was obtained by reaction with *o*-phenylenediamine in the usual manner. This formed bright red needles, m. p. 292—293° (Found: C, 69·3; H, 3·8. $C_{23}H_{14}O_3N_2S$ requires C, 69·3; H, 3·5%).

3 : 4-*Naphthathioxanthone*-1 : 2-*quinone* (VI).—When a solution of the naphthaquinone sulphoxide (V) (1 g.) and freshly fused sodium acetate (5 g.) in acetic anhydride (20 c.c.) was boiled (3 hours),

condensation took place. The brown crystalline cake, remaining after the solvent had been decomposed by water, was purified from acetic acid. The *quinone* was then obtained in orange-brown needles with a metallic lustre, m. p. 244—245°, which were insoluble in alkali (Found: C, 69·8; H, 2·9. $C_{17}H_8O_3S$ requires C, 69·8; H, 2·7%).

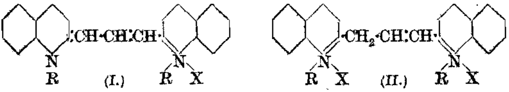
KING'S COLLEGE, LONDON. [*Received, October 26th*, 1928.]

CCCCXVIII.—*Carbocyanine Dyes with Substituents attached to the Three-carbon Chain.*

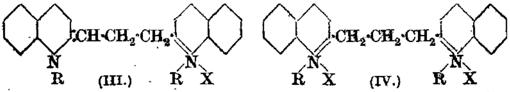
By FRANCES MARY HAMER.

THE *carbocyanine dyes are characterised by the three-carbon chain*, :CH·CH:CH·, linking two heterocyclic nuclei containing nitrogen, which is tervalent in one nucleus, quinquevalent in the other. By varying the nature of these nuclei, seven types of carbocyanine have been made: 2 : 2′-carbocyanine, 2 : 4′-carbocyanine, 4 : 4′-carbocyanine, thiocarbocyanine, oxacarbocyanine, indocarbocyanine (see Hamer, J., 1927, 2796; Bloch and Hamer, *Phot. J.*, 1928, **68**, 21) and selenocarbocyanine (Clark, this vol., p. 2313), whilst, should the nuclei in a given carbocyanine differ from each other (compare Mills and Raper, J., 1925, **127**, 2466), still other possibilities would arise.

There are only three recorded instances of carbocyanines with substituents attached to the three-carbon chain. The earliest is that of the dinitro-derivative obtained by treatment of a 2 : 2′-carbocyanine with nitric acid (Mills and Hamer, J., 1920, **117**, 1550). To the reason cited in the original paper for considering this to be a substitution and not an addition product of the carbocyanine may be added another, based upon a comparison of the stability relationships of two pairs of compounds. In the case of



(I.) (II.)



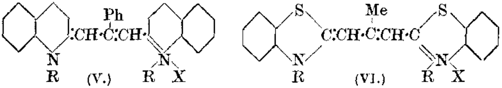
(III.) (IV.)

the first pair, the 2 : 2′-carbocyanine (I) is stable, whilst its monoacid salt (II) is unstable except in the presence of excess of acid. But

with the second pair, the stability relationship is reversed, for the dihydro-derivative (III) of the 2 : 2′-carbocyanine is unknown, whereas the corresponding salts, the methylenediquinaldine dialkylhalides (IV), are stable substances, crystallisable from water (Hamer, J., 1923, **123**, 246). Since the dinitro-compound in question is stable, it is more probably a substitution product of the stable substance (I) than of the unstable dihydro-derivative (III).

Neocyanine is the second instance of a carbocyanine with a substituent attached to the three-carbon chain, since the view has recently been advanced that this dye is a 4 : 4′-carbocyanine in which the hydrogen atom attached to the central carbon of the chain has been replaced by a lepidyl alkylhalide group (Hamer, this vol., p. 1472).

The third case is of especial interest as being a direct synthesis : the carbocyanine (V) was prepared by the action of benzotrichloride on 1-alkyl-2-methylene-1 : 2-dihydroquinoline (Fischer and Rosenhauer, *Z. angew. Chem.*, 1923, **36**, 330 ; Rosenhauer, with Schmidt and Unger, *Ber.*, 1926, **59**, 2356).



(V.) (VI.)

The classic method of carbocyanine preparation, by the action of alkali and formaldehyde on an alcoholic solution of a quinaldinium salt in the presence of a quinolinium salt, gives only negative results when acetaldehyde is used instead of formaldehyde, and carbocyanines containing a methyl group as substituent in the chain have been hitherto unknown. The condensation of quaternary salts, which contain reactive methyl groups, with ethyl orthoformate in the presence of pyridine (Hamer, J., 1927, 2796) gives far better yields of carbocyanines than does any other process ; it seemed possible that similarly by use of ethyl orthoacetate, which is now readily available (Sah, *J. Amer. Chem. Soc.*, 1928, **50**, 516), there might be synthesised a series of carbocyanines possessing the chain :CH·CMe:CH·.

This hope has only been realised in the case of the thiocarbocyanines, with which the ethyl orthoformate and pyridine method is also most successful. By condensing 1-methylbenzthiazole alkylhalides with ethyl orthoacetate in the presence of pyridine, three new dyes of the general formula (VI) were prepared, the yields of pure products varying from 37—53%. Mr. O. F. Bloch has found that these new dyes, like the unsubstituted thiocarbocyanines (compare Mills, J., 1922, **121**, 455), exert a powerful

photographic sensitising action in the green. Their synthesis provides an additional confirmation of the now well-established constitution of the thiocarbocyanines.

When quinaldine ethiodide, or 1-methylbenzoxazole methiodide, was used instead of 1-methylbenzthiazole alkylhalide, the colour changes indicated the formation of a 2 : 2′-carbocyanine and an oxacarbocyanine respectively, but crystalline products were not isolated; the results were still more unfavourable with lepidine ethiodide and 2 : 3 : 3-trimethylindolenine methiodide.

EXPERIMENTAL.

8-Methyl-2 : 2′-diethylthiocarbocyanine Iodide.—1-Methylbenzthiazole ethiodide (2 g.; 2 mols.), dry pyridine (20 c.c.), and ethyl orthoacetate (2·4 c.c.; 4 mols.) were boiled together for ½ hour, during which crystals separated. These were filtered off when cold (1·01 g.; 61% yield) and recrystallised from methyl alcohol (150 c.c.); the yield of dye (0·75 g.) was 45%. The yield is much lower when the condensation is carried out in acetic anhydride solution: 21% yield of crude product, 14% after recrystallisation. For analysis, the dye was dried in a vacuum at 100—120° until of constant weight, and this method of drying was also applied to the other two members of the series (Found: C, 52·3; H, 4·7; I, 25·1. $C_{22}H_{23}N_2IS_2$ requires C, 52·15; H, 4·6; I, 25·1%). The dye formed small, copper-coloured crystals, very different from the large, steely prisms of 2 : 2′-diethylthiocarbocyanine iodide. When it was heated, decomposition began at about 280° and melting occurred at about 290°. The spirit solution shows an absorption band at λ 5400 Å. with a much weaker one at λ 5100 Å., whereas for 1 : 1′-diethylthiocarbocyanine iodide the principal band has its maximum at λ 5600 Å. Like 2 : 2′-diethylthiocarbocyanine iodide, the new thiocarbocyanine behaves in a gelatinobromide emulsion as a powerful sensitiser, giving an almost uniform band, which extends to λ 6400 Å. for moderate exposures, and shows maxima at λ 5900 Å. and λ 5200 Å. The sensitising action of the following two dyes is very similar.

2 : 2′ : 8-Trimethylthiocarbocyanine Iodide.—The crude substance similarly prepared from 1-methylbenzthiazole methiodide (3 g.) was washed with hot water (1·42 g. obtained; 58% yield) and recrystallised from methyl alcohol (1250 c.c.), in which it was only slightly soluble; the yield after recrystallisation (0·91 g.) was 37% (Found: C, 50·4; H, 4·1; I, 26·4. $C_{20}H_{19}N_2IS_2$ requires C, 50·2; H, 4·0; 26·5%). The minute crystals melt at about 298° (decomp.); the principal absorption maximum in spirit solution lies at λ 5400 Å.

salt (I*thyl-2 : 2′-diallylthiocarbocyanine Bromide.*—Similarly from

1-methylbenzthiazole allobromide (2 g.), pyridine (5 c.c.), and ethyl orthoacetate (2·7 c.c.) was prepared a dye (1·13 g.; 63% yield), which on recrystallisation from methyl alcohol (100 c.c.) was obtained in 53% yield (0·95 g.) (Found: C, 59·7; H, 5·0; Br, 16·7. $C_{24}H_{23}N_2BrS_2$ requires C, 59·6; H, 4·8; Br, 16·5%). The blue crystals melt and decompose at about 260°. The principal absorption maximum in spirit solution is at λ 5450 Å.

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ILFORD, E. [*Received, November 5th, 1928.*]

CCCCXIX.—*Surface Oxidation of Aluminium, Tungsten, and Molybdenum.*

By LEONARD CHARLES BANNISTER.

VARIOUS investigators have obtained colours on aluminium anodes and ascribed them to interference tints (Zimmermann, *Trans. Amer. Electrochem. Soc.*, 1904, **5**, 147; Mott, *Electrochem. Ind.*, 1904, **2**, 268), and Tammann (*Z. anorg. Chem.*, 1920, **111**, 78; *et seq.*) has used a similar assumption as a basis for much quantitative work on various colours on metals. Moreover, Evans has obtained evidence in support of this view in the cases of films on lead, iron (*Proc. Roy. Soc.*, 1925, *A*, **107**, 234), and copper (J., 1925, **127**, 2484). On the other hand, the sequence of colours obtained on tungsten by anodic treatment has been attributed by Koerner to the formation of different oxides (*Trans. Amer. Electrochem. Soc.*, 1917, **31**, 221). The present paper aims at reconciling the discrepancies in the cases of aluminium and tungsten and describes the extension of the investigation to the case of molybdenum.

EXPERIMENTAL.

In order to determine whether an optical colour sequence was produced, a film varying regularly in thickness was formed on a single piece of each metal in the following way. The metal, abraded with emery, was made the anode, and a platinum wire used as the cathode. The electrolyte was delivered into the cell in a fine jet of solution, filling it up at a slow but uniform rate. At the same time the voltage was steadily decreased, each successive portion of the metal being thus subjected to a different potential. Examination of the dried anodes showed that on aluminium and on tungsten there had been produced a film which displayed a series of colours, each merging into the next as usual in interference colours. In the case of molybdenum, a strip was placed hori-

zontally in the electrolyte between a cathode and an anode of platinum without making metallic contact with them. After the current had passed for a short time, one half of the strip (the cathodic end) was still quite bright, but the other half was covered with a film which increased in thickness from the centre to the end, and produced a series of coloured bands merging into a black deposit. Therefore, under the influence of a potential gradient, the metals will exhibit an appearance similar to that produced on steel by tempering, which is dependent on a heat gradient.

Heat Tinting in Air.—It is difficult, if not impossible, to obtain on aluminium a colour sequence by heating in air. On tungsten, on the other hand, a sequence was produced by heating one end of a strip and so producing a temperature gradient along it. The thickest part of the film consisted of a black powder which turned yellow in parts after prolonged heating at a higher temperature. The films showing first- and second-order colours, irrespective of the method of production, were extremely hard, and resembled the anodic films of aluminium in this respect. They could be scratched with a diamond, but not with a steel blade; they could be removed with emery paper, but all attempts to obtain a quantity of the substance, by scraping it off the metal, failed owing to the minuteness of the deposit.

In order to preserve the heat tints on molybdenum, a strip of the metal was sealed up in a small glass tube and then heated at one end. The partial pressure of the oxide vapour set up within the tube prevented the resulting oxide film from volatilising, as it does when a piece of the metal is heated in the atmosphere.

When strips of freshly cleaned molybdenum were placed in a solution of potassium hydroxide containing dissolved oxygen, or in a solution of an oxidising agent such as potassium chlorate or nitric acid, the surfaces oxidised at rates depending on the temperature and the concentration of the oxidising solution. No visible films could be obtained by immersion in chromic acid, even at higher temperatures, and, incidentally, this treatment made subsequent oxidation by the other methods a slower process, doubtless owing to passivity caused by the presence of a very thin film, which is much more protective than films of interference thickness.

The colours were temporarily diminished in intensity by immersing the metal strips in liquids of high refractive index, showing that the mechanism is not the selective absorption of light.

It was found that if the thickness of a film were reduced to various extents by immersion for definite lengths of time in solvents, the colour also altered.

The foregoing observations lead to only one conclusion, *viz.*, that the film is an oxide film of variable thickness which can cause interference of light in the visible region of the spectrum and so produce colour.

Anodic Treatment.—A comparison is made of colour with voltage of formation (Tables I and II, for aluminium and tungsten, respectively) and with the number of coulombs (Tables III and IV). For aluminium it is possible to calculate the refractive index of the film.

TABLE I.

Anodic treatment of aluminium in $Na_2HPO_4,12H_2O$ (satd.) at 17°.

Voltage.	Colour.
40— 59	Pale yellow.
59— 69	Brown.
69— 77	Red.
77— 85	Purple.
85— 93	Blue.
93—107	Green.
107—120	Yellow.

TABLE II.

Anodic treatment of tungsten in *N*-KCl at 17°.

Voltage.	Colour.
10—21	Yellow.
21—25	Crimson.
25—28	Violet.
28—36	Dark blue.
36—56	Light blue.

TABLE III.

Aluminium (Area of anode, 38·05 sq. cms.).

Coulombs passed.	Thickness of Al_2O_3.	Colour observed.	Approx. wave-length of light missing.	Refractive index.
3·57	0·075 μ	Straw.	0·42 μ	1·73
4·14	0·087 μ	Brown.	0·46 μ	1·60
4·96	0·104 μ	Purple.	0·51 μ	1·59
6·50	0·136 μ	Violet.	0·56 μ	1·52

The values in the fourth column are the wave-lengths of the light complementary to the colour observed. The values obtained for the refractive index are in fairly good agreement with Cauchy's dispersion formula for transparent substances.

TABLE IV.

Tungsten (Area of anode, 4·0 sq. cms.).

Anodic treatment at 143 volts and 16°.

(*a*) In *N*-KCl.				(*b*) In *N*/100-KCl.	
Total coulombs.	Colour.	Total coulombs.	Colour.	Total coulombs.	Colour.
1·48	Yellow.	16·28	Blue.	0·275	Pale yellow.
2·96	Orange.	23·68	Pale green.	0·543	Crimson.
4·44	Purple.	26·64	Green.	0·803	Blue.
5·92	Crimson.	34·04	Deep yellow.	1·056	Light blue.
7·40	Violet.	41·44	Orange.		
11·84	Deep blue.				

Table IV shows that the process of film formation is more efficient when the conductivity of the electrolyte is considerably reduced.

Even if the specific gravity of the film were known, it would not b legitimate to determine the thickness from the amount of electricit passed, for the proportion of current used in film formation seem to vary with the concentration of the electrolyte, hence the refractiv index of the film on tungsten is unknown.

The tables given by Koerner clearly indicate that his experiment were not conducted over a sufficiently wide range of conditions t lead to accurate conclusions. The evidence available suggests tha the oxide is one lower than WO_3.

The Isolation of the Film.—By the method of Whitey and Mills (*J. Soc. Chem. Ind.*, 1926, **45**, 170T), the films on aluminium wer isolated from their metallic base by volatilisation of the latter in stream of hot hydrogen chloride, special precautions being taken t ensure the absence of traces of water vapour and air during th operation, for otherwise a white, chalky film of alumina was pro duced. Many of the specimens of film-covered aluminium showe a peculiar inertness towards the attacking gas, but it was observe that the reaction could be initiated by increasing the velocity of th current of gas. Unfortunately, the method was quite unsuccessfu in isolating films from tungsten and molybdenum.

The phosphate content of the films was found to vary somewhat in some, none was detected, and in others it was present up to 6% It seems probable, therefore, that when phosphate or other aci radical is present, it is merely occluded or held in suspension withi the pores of the film. When the films were heated to redness, a los in weight of 4% took place, which indicates that they consist mainl of oxide with perhaps some water which became sealed within the pores during their growth.

The values for the ratio (Increase of anode weight during trea ment)/(Weight of isolated film) were found to be 0·63, 0·58, 0·5 and 0·55 for four different anodes, whereas the theoretical valu for O_3/Al_2O_3 is 0·47.

It may be noted that Sutton and Willstrop (*J. Inst. Metals*, 192 **38**, ii, 259) have analysed the films formed on aluminium by standar anodic treatment in chromic acid, and have found them to consi of the oxide together with a trace of chromate.

The author wishes to thank Prof. W. C. McC. Lewis, F.R.S., b whose kind permission this work was done, Mr. W. J. Shutt, M.Sc for practical advice, and also Mr. U. R. Evans, M.A., with whoi subsequent discussion has been of great value.

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CCCCXX.—*Studies of Dynamic Isomerism. Part XXVIII. Absorption Spectra of the Ketonic and Enolic Forms of an α-Diketone.*

By Thomas Martin Lowry, Henri Moureu, and Charles Alexander Hamilton MacConkey.

In the preceding paper of this series (this vol., p. 1333), the statement of Morton and Rosney (*J.*, *1926*, *706*) that "the isomeric forms of benzoylcamphor give bands of the same wave-length, but of unequal intensity" was shown to be incorrect, since the absorption bands actually occur at different wave-lengths, although they are of very similar intensity, when examined before isomeric change has taken place. Since the preceding statement was used as evidence in support of the general proposition "that enolic and ketonic modifications possess the same wave-length of maximum absorption," it was of interest to see whether this proposition could be substantiated in other cases. In the present investigation, therefore, we have taken advantage of the separation by one of us (Moureu, *Compt. rend.*, 1928, **186**, 380) of the ketonic and enolic forms, (I) and (II), of benzylmethylglyoxal, in order to repeat with an α-diketone the tests that had already been carried out on a typical β-diketone.

$$\underset{\text{(I; ketonic form.)}}{C_6H_5\cdot CH_2\cdot CO\cdot CO\cdot CH_3} \rightleftharpoons \underset{\text{(II; enolic form.)}}{C_6H_5\cdot CH{:}C(OH)\cdot CO\cdot CH_3}$$

The labile ketonic form (I) of benzylmethylglyoxal can be separated in a pure state as a yellow liquid by distillation in presence of a trace of sodium carbonate. Under these conditions, a reversible reaction is produced in the liquid phase, but the more volatile isomeride (which resembles the *o*-quinones in this property) escapes and becomes fixed in the vapour phase by the elimination of the non-volatile catalyst. It therefore distils as a homogeneous product, b. p. 104°/10 mm., and when frozen melts sharply at 17°. On the other hand, when an alkali or a nitrogenous base is added to the liquid, the enolic form (II) crystallises in a pure state, since it is the stable solid phase at all temperatures up to its m. p. at 70°. In the absence of a catalyst, the enol also can be distilled without change, boiling at 134°/10 mm.

The structures of the two isomerides were established by the fact that the yellow quinone-like ketonic form gave no reaction with bromine, reacted but slowly with ferric and antimonous chlorides, and gave only an 18% yield of methane when acted on by the Grignard reagent, whereas the colourless enolic form immediately fixed one molecular proportion of bromine, formed a brown

salt with ferric chloride and a crystalline derivative with antimonous chloride, and gave an 80% yield of methane with the Grignard reagent (*Compt. rend.*, 1928, **186**, 503).

The measurements set out below show that the absorption bands of the ketonic and enolic forms of the α-diketone differ even more widely than in the case of the stable and labile forms of the β-diketone. In particular, the two adjacent carbonyl groups in the α-diketone displace the familiar ultra-violet band of the simple ketones into the visible region, exactly as in the case of camphorquinone (Lowry and French, J., 1924, **125**, 1921), but without increasing its intensity, whereas the conjugated double bond of the enolic isomeride gives rise to an enormous increase of intensity, but without any important change of wave-length, exactly as in the case of benzylidenecamphor (*ibid.*). The inequality of wave-length is therefore twice as great as in the case of benzoylcamphor, and is accompanied by a difference of intensity in the ratio of about 600 to 1.

The structures assigned to the two isomerides are largely irrelevant to the present discussion, since the general proposition cited above implies that, if a series of isomerides can be converted into one another by successive keto-enol transformations, the wave-length of the absorption bands must remain constant throughout, whatever structure may be assigned to individual members of the series. If, therefore, two isomeric enols can be produced from a given ketone, or if two stereoisomeric enols can be converted into one another through an intermediate ketonic form, as might conceivably occur in the case of benzoylcamphor (*loc. cit.*, p. 1334), the absorption bands of both enols must be at the same wave-length as that of the ketone, and must therefore be identical in wave-length with one another. In the present instance, however, the quinone-like colour of the liquid diketone and the absence of quinonoid characters in the solid isomeride provide an ocular vindication of the structures deduced from the chemical diagnosis recorded above, and make it obvious that we are dealing with a typical keto-enol isomerism.

In view of their close relation to the α-diketone, we have also included in our programme the measurement of the absorption spectra of the compounds set out below.

$C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3 \rightleftharpoons C_6H_5{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH_3$

(III; Benzoylacetone, ketonic form.) (IV; Benzoylacetone, enolic form.)

$C_6H_5{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3$ (V; Benzylideneacetone.)

$C_6H_5{\cdot}\overset{\frown O \frown}{CH{\cdot}CH}{\cdot}CO{\cdot}CH_3$ (VI; Acetylphenylethylene oxide.)

Benzoylacetone is a structural isomeride of the α-diketone which

forms the main subject of the present investigation. It exhibits the dual reactivity of a tautomeric compound, yielding derivatives of the ketone (III) and of the enol (IV); but, unlike the isomeric α-diketone, it is only known in one form, to which the structure (IV) is conventionally assigned. The unsaturated ketone (V) has been examined on account of its close relationship to the isomeric enols (II) and (IV). The ethylenic oxide (VI) is a compound of fixed structure, which is isomeric with the labile α- and β-diketones (I) and (III), and the enols (II) and (IV), to which it is related in the same symmetrical manner as the olefin from which it is derived.

FIG. 1.

Molecular extinction coefficients of benzoylacetone. (a) In alcohol; (b) in cyclohexane.

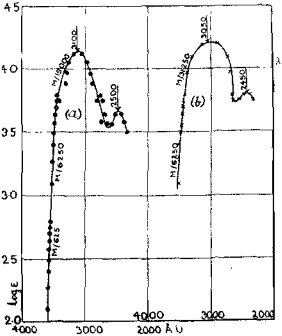
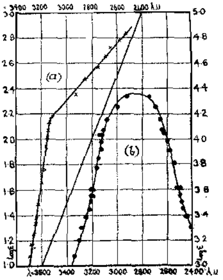


FIG. 2.

(a) *Molecular extinction coefficients of acetylphenylethylene oxide.*
(b) *Molecular extinction coefficients of benzylidencacetone.*



1. *Benzoylacetone*.—The absorption spectrum of benzoylacetone has been examined by Baly and Desch (J., 1905, **87**, 766) and by Morgan and Moss (J., 1913, **103**, 78), who recorded the presence of a single absorption band. Our own measurements, with alcohol as the solvent [Fig. 1 (*a*)], gave two maxima

$$\log \varepsilon = 4{\cdot}15 \text{ at } 3100; \ \log \varepsilon = 3{\cdot}66 \text{ at } 2500 \text{ Å.U.},$$

which we had no difficulty in identifying with the characteristic bands of the two forms of benzoylcamphor, *viz.*, $\log \varepsilon = 4{\cdot}27$ at 3140; $\log \varepsilon = 4{\cdot}21$ at 2420 Å.U. No change was observed in the absorption spectrum when examined ½ hour after the preparation

of the solution and again on the following day. A similar pair (maxima

$$\log \varepsilon = 4{\cdot}26 \text{ at } 3050; \ \log \varepsilon = 3{\cdot}80 \text{ at } 2450$$

was observed when the experiment was repeated with a freshly prepared solution in *cyclo*hexane [Fig. 1 (*b*)], the measurements bein completed in the course of about 80 minutes.

Since the only known form of benzoylacetone gives an immediat coloration with ferric chloride, it has generally been supposed t have an enolic structure, and the band observed by Baly and Desch and by Morgan and Moss at 3100 Å.U., has been regarded as characteristic of the isomeride (IV). If no other information wer available, it might be supposed that the two bands shown in Fig. (*a*) and (*b*) were both due to the same isomeride, since we have no been able to observe them separately. On the other hand, th close agreement of the wave-lengths of the bands of Fig. 1 (*a*) witl those of alcoholic solutions of the two forms of benzoylcampho leads us to conclude that in this case also the bands are due to tw isomeric forms of the β-diketone; our failure to separate them ca then be attributed to catalysis, since we do not yet know of any certain method of arresting isomeric change in these very sensitiv prototropic compounds. This conclusion is confirmed by the fac that, whilst the intensity of the bands given by the two pure form of benzoylcamphor is greater than those of the two bands of benzoyl acetone, the latter agree quite well with the intensities of the hand ($\log \varepsilon = 4{\cdot}10$ and $3{\cdot}90$) in an equilibrium mixture of the two form of benzoylcamphor. According to this view, the crystals of benzoyl acetone, melting at 61°, may be regarded as a homogeneous solid phase, probably corresponding in structure with the stable form o benzoylcamphor, but reverting with even greater readiness to ar equilibrium mixture in solution.

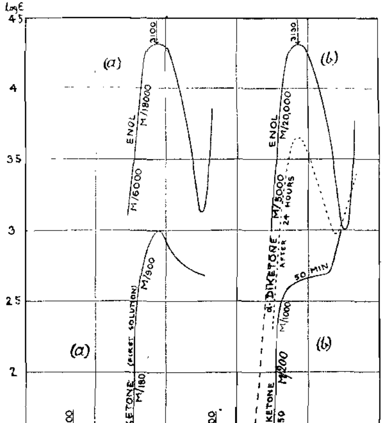
2. *Benzylideneacetone and Acetylphenylethylene Oxide*.—The absorption spectrum of benzylideneacetone (V) is shown in Fig. 2 (*b*). As might be expected, it gives a maximum, $\log \varepsilon = 4{\cdot}36$ at 2850 Å.U., in close agreement with the maximum ($\log \varepsilon = 4{\cdot}32$ at 2900 Å.U.) already recorded for an alcoholic solution of benzylidene-camphor (Lowry and French, J., 1924, **125**, 1921). The close agreement in the position and intensity of the two bands shows that the influence of the camphor nucleus is not very great, and suggests that the observations made with camphorquinone, benzoylcamphor, and other compounds of the camphor group may be expected to reappear almost unchanged in the corresponding open-chain compounds of the present series.

The absorption spectrum of acetylphenylethylene oxide is shown Fig. 2 (*a*). Unlike the preceding compound, it does not give an

absorption band, but only a rapid " step-out " at wave-lengths less than 3100 Å.U. Since one of the ketonic groups remains intact when we pass from the labile α- or β-diketone to the fixed oxide, it is remarkable that this oxide does not give the familiar ketonic band at about 3000 Å.U. An explanation may perhaps be found in the view that, in the absence of a conjugated double bond, the

FIG. 3.

Molecular extinction coefficients of benzylmethylglyoxal in alcohol.
(a) *First series ;* (b) *second series.*



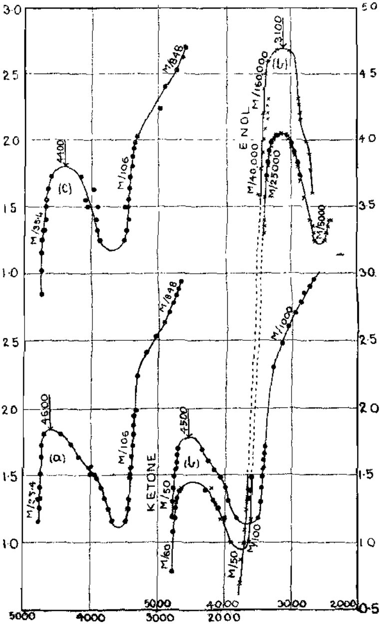
" ether " oxygen atom becomes interlocked with the ketonic oxygen, in much the same way as in the esters, so that the oxide may be regarded as an analogue of benzyl acetate rather than of acetophenone.

3. *Benzylmethylglyoxal and its Enolic Isomeride.*—(a) *Solid form.* The molecular extinction coefficients of the crystalline form of the α-diketone in alcoholic solution are set out in Fig. 3. Unlike the

isomeric β-diketone (benzoylacetone), this compound gives only single *maximum*, log ε = 4·3 at 3100 Å.U., corresponding close with that of the stable form of benzoylcamphor, whilst a very stro

Fig. 4.

Molecular extinction coefficients of benzylmethylglyoxal. (a) *In cyclohexan (first series)*; (b) *in cyclohexane (second series)*; (c) *in chloroform.*



● = *Solutions prepared from ketone.*
× = ,, ,, ,, *enolic isomeride.*

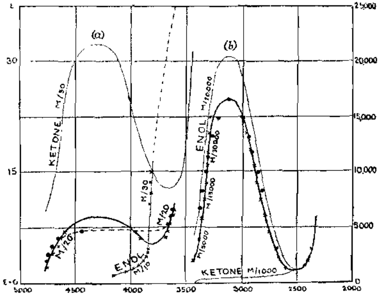
minimum, log ε = 3·2 at 2480 Å.U., appears at the wave-leng of the absorption band of the labile form of the latter compour A duplicate determination gave a similar maximum, log ε = 4·3

3130 Å.U., but a slightly deeper minimum, extending to log ε = 3. Since the solid and its freshly prepared solutions were quite colourless, it is clear that the enolic form does not give an absorption band in the visible spectrum; but this was also shown by direct observations at concentrations of *M*/10 and *M*/30, which are plotted at the foot of Fig. 5 (*a*).

A solution in *cyclo*hexane [Fig. 4 (*b*)] showed an even stronger maximum, log ε = 4·7 at 3100 Å.U., but the curve was not followed as far as the minimum, which occurs at 2500 Å.U. in the equilibrium mixture (see below). On the other hand, the absence of an absorption band in the visible region was again established by direct

FIG. 5.

Equilibrium of ketonic and enolic forms of benzylmethylglyoxal in alcohol.
(a) *Ketonic band;* (b) *enolic band.*



● = *Solutions prepared from ketone.*
× = " " " *enolic isomeride.*

observations, since an *M*/50-solution showed an extinction coefficient which was already less than 5 (log ε = 0·7) at 3750 Å.U., and the absorptive power of the solution was then still diminishing according to an almost linear law as the wave-length was increased.

It is of interest to compare the bands at about 3100 Å.U. of the enolic forms of the α- and β-diketone with the bands of benzylideneacetone at 2850, and of benzylidenecamphor at 2900 Å.U. It appears certain that we are dealing throughout with the same band, but that it is displaced to a slightly longer wave-length by the introduction of the hydroxyl radical, in just the same way as the ketonic band of camphor is displaced towards the visible region by the introduction of a halogen in the α- or α′-position (Lowry and

Owen, *J.*, 1926, 606; compare also Grossmann, *Z. physikal. Chem.*, 1914, **109**, 329, 337). This band, although it is given by two isomeric enols, is in no sense a characteristic "enolic" band, since it is equally well developed in benzylideneacetone and benzylidenecamphor, although the hydroxyl group of the enol is absent in these two compounds; it appears, indeed, to be merely the ketonic band reinforced by conjugation of the carbonyl double bond with an olefinic double bond, exactly as in methylenecamphor (Lowry and French, *J.*, 1924, **125**, 1921).

(b) *Liquid form.* The liquid form of the diketone reverts very easily to the crystalline form, since the yellow liquid solidifies almost immediately in the presence of a trace of a nitrogenous base. We were therefore less confident of securing an independent record of the ketonic band, especially in view of the very remarkable absorptive power of the isomeric enol. From analogy with camphorquinone, we anticipated that this band would be found in the blue region of the spectrum at about 4700 Å.U., and at a relatively high concentration, say, $\log \varepsilon = 1{\cdot}8$. We therefore made our first measurements with an $M/35{\cdot}4$-alcoholic solution, and observed the expected maximum, $\log \varepsilon = 1{\cdot}5$ at 4300 Å.U. [Fig. 3 (*a*)]. On diluting the solution, however, we found that a second maximum had already been developed in the ultra-violet at 3120 Å.U., although its intensity, $\log \varepsilon = 2{\cdot}97$, was 20 times weaker than in the case of the pure enol. We therefore repeated the experiment, taking much greater care in order to complete our observations before isomeric change had begun. The results of the second experiment, in which the exposures were completed in 50 minutes from the time when the solution was prepared, are shown in Fig. 3 (*b*). The curve no longer shows a maximum in the ultra-violet, but only a "step-out," $\log \varepsilon = 2{\cdot}6$ to $2{\cdot}8$ at 3300 to 2700 Å.U. This step-out is probably a genuine characteristic of the pure α-diketone, since it is very similar to one that had already been recorded in the case of camphorquinone (Lowry and French, *J.*, 1924, **125**, 1921), where enolisation would appear to be impossible (Bredt, *J. pr. Chem.*, 1918, **97**, 1; *Annalen*, 1924, **437**, 1), since it would involve bending all the four bonds of the carbon atom (4) in the direction of the carbon atom (10) of the camphor nucleus. The step-out can also be compared with the *one* now recorded in the isomeric acetylphenylethylene oxide (VI), and may perhaps be attributed to the skeleton $C_6H_5{\cdot}C{-}C{-}CO{-}CH_3$ (with —O— bridging the two C atoms) which is common to both isomerides.

...firmation of these results was obtained by making use of of the ...s in *cyclo*hexane, for which molecular extinctions are plotted A duplic...*a*). The curves again show a maximum ($\log \varepsilon = 1{\cdot}85$ at

4600 Å.U.) in the visible spectrum, a *minimum* (log ε = 1·2 at 3600 Å.U.), and a step-out at wave-lengths on either side of 3000 Å.U. A duplicate series of observations, which are plotted in Fig. 4 (*b*), gave a precisely similar curve, although the numerical values are not quite the same in the two series. The two curves agree, however, in suggesting that the band in the visible spectrum is unsymmetrical, since each curve rises almost vertically on the side of longer wave-lengths, but spreads out on the side of shorter wave-lengths, as if there were a second characteristic frequency at about 4000 Å.U.

The molecular extinction coefficients of a solution of the α-diketone in chloroform, which are set out in Fig. 4 (*c*), show the same essential characteristics, *viz.*, a maximum (log ε = 1·8 at 4400 Å.U.) in the visible spectrum, followed in the ultra-violet by a minimum (log ε = 1·2 at 3700 Å.U.), and a step-out at wave-lengths on either side of 3000 Å.U., but without any indication of a maximum at 3100 Å.U.

The principal interest of these observations is the complete separation, which has again been realised, of the characteristic absorption bands of the enolic and ketonic isomerides. Thus, on the one hand, the colourless enol is completely transparent in the region covered by the visible absorption band of the α-diketone; on the other hand, it shows no sign of the band of shorter wave-length, which is given by the labile form of benzoylcamphor, and which appears again in the absorption spectrum of benzoylacetone. Conversely, the liquid diketone, which owes its yellow colour to the presence of a characteristic quinonoid band in the blue region of the spectrum, has been dissolved in three different solvents without developing a second maximum in the ultra-violet. Each isomeride therefore retains its individuality in solution and gives rise to an absorption band of characteristic wave-length, in close agreement with the wave-length predicted from the study of compounds of analogous structure.

4. *Equilibrium Mixtures.*—On account of the remarkable absorptive power of the enolic isomeride, special care had to be used in preparing solutions of benzylmethylglyoxal, in order to avoid the development of an ultra-violet maximum, resulting from incipient enolisation of the α-diketone. Nevertheless, the pure compound is much more stable than the majority of substances in which prototropic change is liable to take place, since the yellow liquid can be kept in hard-glass tubes for many weeks without showing any signs of solidification,* although this can be induced immediately by the addition of a basic catalyst. The stability of the α-diketone

* Measurements of refractive index show that a slow transformation takes place even in hard-glass tubes.

ıd its enolic isomeride is indeed much greater than that of the two rms of benzoylcamphor, although these have been selected peatedly for experiments on reversible isomeric change on account the readiness with which the two isomerides can be prepared and ›pt. It was, however, only when we tried to prepare equilibrium ixtures of identical properties from the enolic and ketonic forms benzylmethylglyoxal that we discovered with what difficulty the ansformation is brought about in solution.

In the first instance, solutions of the two isomerides were allowed stand for several days, since this had always proved sufficient to 'oduce a condition of equilibrium in the case of benzoylcamphor. 'hen dissolved in *cyclo*hexane, however, the α-diketone and its ıolic isomeride had the same intensities of selective absorption 'en after the solution had been kept for several days. A trace of peridine was then added, by stirring the solution of the enol with platinum wire which had been dipped into the liquid base and ained against the side of the vessel; but even this deliberate ldition of a catalyst produced no alteration in the absorptive ›wer of the solution. Solutions of the two isomerides in *cyclo*-›xane were next prepared, containing 1 mol. of piperidine for 'ery 100 mols. of the organic compound. After 20 hours, a slight ›crease was observed in the absorptive power of the ketonic form the visible region. In the meanwhile, the enolic form had veloped an absorption band in the visible spectrum at λ 4500, of ›ensity $\varepsilon = 12{\cdot}5$, as contrasted with $\varepsilon = 60$ for the pure ketone d $\varepsilon = 30$ for the equilibrium mixture finally obtained; but the 'sorptive power of this solution was unchanged after a further riod of 5 days, although the ketonic and enolic solutions were ll far removed from equality in this respect. These two solutions re then kept in a thermostat at 28° for 24 hours, but a glance owed that they were still of quite different depths of colour. In ler to provide an amphoteric catalyst, a solution of *p*-cresol in *lo*hexane was now added to each solution, in quantity such that ə molar concentrations of piperidine and *p*-cresol were equal in ə resulting mixture. The maximum absorptive power of the tonic solution in the visible spectrum at λ 4500 fell to $\varepsilon = 30$, but ıt of the enol at the same wave-length was not altered by this lition of cresol, but remained constant at λ 12·5. When diluted, ə solution of the enol gave $\varepsilon = 5000$ at λ 3150, whilst the solution the ketone gave $\varepsilon = 60$, but in neither case was a definite absorp-n band developed.

Equilibrium mixtures which gave identical extinction coefficients re finally obtained by adding 1 mol. % of piperidine to the dis-ved ketone or enol and keeping the solutions for 20 hours in

›sed flasks at 50°. The equality of visual colour of the two lutions was confirmed by measurements with a Kletz colorimeter ;ainst a solution of camphorquinone. The results were as follows :
In *cyclo*hexane :

$$\frac{\text{Camphorquinone, } M/60}{\text{Ketonic solution, } M/20} = 1{\cdot}88,\ 1{\cdot}92. \quad \text{Mean} = \mathbf{1{\cdot}90}.$$

$$\frac{\text{Camphorquinone, } M/60}{\text{Enolic solution, } M/20} = 1{\cdot}81,\ 1{\cdot}92. \quad \text{Mean} = \mathbf{1{\cdot}87}.$$

In ethyl alcohol :

$$\frac{\text{Camphorquinone, } M/180}{\text{Ketonic solution, } M/20} = 0{\cdot}96,\ 0{\cdot}99,\ 0{\cdot}96,\ 1{\cdot}03. \quad \text{Mean} = \mathbf{0{\cdot}98}.$$

$$\frac{\text{Camphorquinone, } M/180}{\text{Enolic solution, } M/20} = 1{\cdot}00,\ 0{\cdot}88,\ 0{\cdot}97,\ 0{\cdot}94. \quad \text{Mean} = \mathbf{0{\cdot}95}.$$

ıe equilibrium mixture in *cyclo*hexane has therefore rather more an one-sixth of the intensity of colour of camphorquinone, whilst ethyl alcohol the ratio is rather more than one-ninth; but, since is ratio depends on the width of the bands, as well as on their ›ensity, it cannot be used to deduce the ratio of the maximum tinction coefficients, as measured with a spectrophotometer.

Quantitative data for the molecular extinction coefficients of lutions in *cyclo*hexane are shown in Fig 4 (*b*), and those of alcoholic lutions are shown in Fig. 5, where different scales of intensity are ›d for the visual region of the ketonic band and for the ultra- ›let region of the enolic band. In each case the circles represent lues recorded for solutions of the ketone itself, and crosses are ›d for solutions prepared from the enolic isomeride. The two ›ies of data can be represented by a single curve for each solvent, › largest deviation being at the ketonic band of Fig. 5 (*a*), where › solution of the enol showed a shallow maximum and minimum, ıereas the solution prepared from the ketone gave only a step-out; › points on either side of the loop can, however, be plotted on a gle curve.

The circumstances in which these experiments were made were t suitable for deducing the equilibrium proportions of the ketonic d enolic forms, since the conditions of equilibrium were not well fined, and the dilutions at which the ketonic and enolic bands re observed differed very widely. It is therefore not surprising ıt the proportion of ketone (about $\frac{1}{2}$) in *cyclo*hexane at a dilution $M/60$ and of enol (about $\frac{1}{4}$) in the same solvent at a dilution of $/25{,}000$ do not add up to unity. In the case of the alcoholic utions, the proportions of ketone and enol deduced from the ›inction coefficients at the wave-lengths of the two maxima are ıghly $\frac{1}{4}$ and $\frac{4}{5}$ at dilutions of $M/20$ and $M/30{,}000$, respectively;

n this solvent, therefore, there appear to be 3 or 4 parts of enol to one of ketone, but this ratio also is rendered uncertain by the widely different concentrations at which the proportions of ketone and enol were determined, and by deviations from Beer's law, which are shown by the varying width of the absorption bands as observed in solutions of different concentrations. Attention should also be directed to the fact that at the wave-length λ 3800, at which the enol and the ketone have the same extinction coefficient, $\varepsilon = 15$, in alcoholic solutions, the equilibrium mixture has an absorption coefficient which is only about half as great. This anomaly throws doubt on the validity of the additive law as applied to mixtures of the α-diketone and its enolic isomeride, and suggests that they may perhaps unite with one another (like quinol and quinone) to form an unstable complex in solution.

Although the proportions of the isomerides cannot be deduced with certainty from the absorption curves for the equilibrium mixtures, these curves provide very important evidence as to the qualitative composition of these mixtures. Thus, if the two absorption bands of benzoylacetone, or of the two forms of benzoylcamphor, were characteristic of a pair of stereoisomeric enols, it would be difficult to exclude the possibility of a similar stereoisomerism in the enolic form of the α-diketone, as may be seen by comparing the formulæ

$$\begin{matrix}C_6H_5 \\ H\end{matrix}\!>\!C{=}C\!<\!\begin{matrix}OH \\ CO{\cdot}CH_3\end{matrix} \quad \text{and} \quad \begin{matrix}C_6H_5 \\ HO\end{matrix}\!>\!C{=}C\!<\!\begin{matrix}H \\ CO{\cdot}CH_3\end{matrix}$$

α-Enol. β-Enol.

Actually, however, the absorption curves for equilibrium mixtures of the two forms of benzylmethylglyoxal give no indication of the maximum at λ 2450, which is characteristic of the labile form of benzoylcamphor, and which is also seen in the absorption spectrum of benzoylacetone. On the contrary, the curves for solutions in alcohol and in *cyclo*hexane actually pass through a *minimum* in this region of the spectrum. The band at λ 2450 must therefore be associated with a structure which is not only different from those of the two known forms of benzylmethylglyoxal, but is not produced from either of them by isomeric change in presence of a catalyst. Such a form cannot be a mere stereoisomeride, although it might conceivably be a co-ordinated enol, containing a 6-atom ring which could not be produced from an α-diketone.

Summary.

Eqtnnzylmethylglyoxal, $C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}CO{\cdot}CH_3$, shows an absorptio were finall the visible spectrum, with a maximum log $\varepsilon = 1{\cdot}5$ at 430 solved ketol, or log $\varepsilon = 1{\cdot}85$ at 4600 in *cyclo*hexane, but only a "ste

out " in the ultra-violet at about 3000 Å.U. The enolic isomeride, $C_6H_5 \cdot CH:C(OH) \cdot CO \cdot CH_3$, on the other hand, is colourless, but has a strong absorption band in the ultra-violet with a maximum log ε = 4·3 at 3100 in alcohol, or 4·7 at 3100 in *cyclo*hexane. Both bands are given by solutions in which the two isomerides are in equilibrium.

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CCCCXXI.—*Studies of Valency. Part XII. Isomeric Derivatives of Diethyl Telluride.*

By FRANK LATHE GILBERT and THOMAS MARTIN LOWRY.

VERNON'S last paper on " Organic Derivatives of Tellurium " concludes as follows : " There is still much work to be done on this subject, and it would be of interest to find out whether other aliphatic derivatives, such as *diethyltelluronium di-iodide*, also exist in two isomeric forms. The reason that no further investigation is being undertaken is entirely due to the intolerable nature of tellurium and its derivatives " (J., 1921, **119**, 696). The present paper describes the completion of the investigation which Vernon contemplated, but was not able to undertake. This investigation has led to the discovery that diethyl telluride, like the dimethyl compound, yields two series of isomeric salts, and that these are derived from two isomeric bases, which are related to one another in precisely the same way as the α- and β-bases of the dimethyl series. This result was by no means a foregone conclusion, since the cyclic base prepared by Morgan and Burgess (this vol., p. 321) does not undergo isomeric change when evaporated to dryness (Gilbert and Lowry, this vol., p. 2658), although the di-iodide exists in two enantiotropic forms; and Mr. W. H. Mills has informed us that the diphenyl compound also shows no analogous transformation when treated in the same way as the dimethyl base. The isomeric derivatives now described therefore provide the first experimental justification for the view that the isomerism discovered by Vernon is not restricted to the methyl compounds, and may be a general property of the dialkyltelluronium bases and salts.

The salts in which this isomerism has been detected have been known for nearly a century. They were prepared by Wöhler (*Annalen*, 1840, **35**, 111; 1852, **84**, 73; 1855, **93**, 233) and by Mallet (*ibid.*, 1851, **79**, 223) by oxidising diethyl telluride to the dinitrate, $TeEt_2(NO_3)_2$, by the action of nitric acid. From this salt

the chloride, bromide and iodide, the sulphate and oxalate, the oxide and the oxyhalides were obtained, but without any indication of isomerism or of isomeric change. Vernon prepared the α-di-iodide, $TeEt_2I_2$, by the action of ethyl iodide on metallic tellurium and analysed the product; it melted at 57°, whereas Wöhler gives the m. p. as 50°. He also prepared the base by the action of silver oxide on the iodide, and added that "If this base does not decompose when its solution is evaporated to dryness, but gives diethyltelluronium oxide, *the existence of two haloid series would be highly* probable." Our first attempt to verify this prediction gave rise to *diethyltellurone*, $TeEt_2O_2$, by spontaneous oxidation of the base, whereas the α- and β-dimethyl bases and Morgan's cyclic base are only oxidised to the tellurone by boiling with hydrogen peroxide; but by evaporating a solution of the α-base to dryness in an atmosphere of nitrogen, a substance was obtained which gave in aqueous solution quite different reactions towards silver nitrate and hydriodic acid and evidently contained the isomeric β-base. From this substance a characteristic series of β-salts was prepared.

The two series of isomeric salts correspond very closely with those of the dimethyl series. Thus the α-di-iodide differs from the β-compound in that it is freely soluble in chloroform, and can be converted into a tetra-iodide. The remarkable contrast which Vernon observed between the action of alkalis on the α- and β-salts was also repeated in the diethyl series. Thus, the α-di-iodide gave rise to an *oxyiodide*, $I[TeEt_2{\cdot}O{\cdot}TeEt_2]I$, although this was produced under a wider range of conditions than in the methyl series, since the same product was obtained when we tried to prepare the ethyl analogue of Vernon's beautifully crystalline α-dimethyltelluronium dioxyiodide. The β-di-iodide, on the other hand, was converted by the action of alkali into a salt having the characteristics and the approximate composition of a *triethyltelluronium iodide*, $TeEt_3I$.

A remarkable contrast is found in the fact that the α- and β-chlorides and bromides of the diethyl series are obtained as oils, whereas those of the dimethyl series are crystalline solids of fairly high melting point. A close analogy (comparable with that which has already been pointed out in connexion with the conductivities; this vol., p. 314) is found, however, in the trialkylstibine series, where the trimethylstibine dihalides are all solid, as is also the triethylstibine di-iodide, whereas the triethylstibine dichloride and dibromide are liquids.

Apart from this contrast in melting points, the physical properties of the diethyl compounds are in general such as we should have expected in the light of our observations on the dimethyl series. For instance, the absorption spectra of the iodides all show the

twin maxima of the "iodoform band," and the bromides exhibit only a step-out. Again, measurements of molecular conductivity show that, when dissolved in water, the dihalides lose one atom of halogen by hydrolysis to the free acid, giving rise to hydroxy-halides, to which the general formula $[TeEt_2{\cdot}OH]X$ is assigned. The only compound of the group which has been isolated is, however, the α-oxyiodide, $I[TeEt_2{\cdot}O{\cdot}TeEt_2]I$. The hydroxy-halides are ionised more or less completely in aqueous solution, but are not hydrolysed even in dilute solutions from which the excess of acid has been removed. As in the methyl series, they are acid rather than alkaline in their reaction.

An interesting comparison can be made between the properties of the α- and the β-base. As in the dimethyl series, the β-base has a higher conductivity than the isomeric α-base, and it is also shown by potentiometric titrations to be stronger than the α-base during the first half of the process of neutralisation. At this stage, however, the curves cross, so that the β-base is seen to be weaker than the α-base after half-neutralisation. The crossing of the curves is due to the fact that, whilst the α-base gives a neutralisation curve of the normal type, the curve for the β-base is inflected, exactly as in the case of the α-dimethyl base (this vol., p. 1997), although not to such a marked extent. The reappearance of this inflected curve in the case of the β-base, and the absence of any inflexion in the curve for the α-base, provide the most striking evidence of the persistent analogy between the methyl and ethyl series of compounds.

EXPERIMENTAL.

α-Diethyltelluronium Di-iodide.—Precipitated tellurium (crushed crystalline tellurium is less effective) is heated in Carius tubes for 10 days at 100° with ethyl iodide (2 mols.), the tubes being shaken every 12 hours. Very little pressure is developed, even at 100°, and there is no pressure when the tubes are opened. Since the compound has been found to decompose slightly during fusion, it would probably be better to heat at 40—50° during a period of perhaps 20 days, so that the compound is not prepared in the fused state. The di-iodide was extracted with hot chloroform (instead of with alcohol, as recommended by Vernon), filtered through a hot funnel to remove unchanged tellurium, and separated by rapid evaporation. It was obtained from alcohol in large brownish-red crystals, m. p. 57°; yield, about 20%. The final product was identical in all respects with a specimen left by Vernon.

The *α-tetraiodide*, $TeEt_2I_4$, was obtained as a black residue on mixing a violet solution of iodine and a yellow solution of the α-di-iodide in chloroform, and refluxing the mixture for one minute,

the colour almost wholly disappearing; but some decomposition occurred in this process, giving rise to free iodine and tellurium. The α-tetra-iodide was also formed when hydriodic acid was added to a solution of the α-base, which had been partly oxidised by boiling with hydrogen peroxide for a few minutes, and then filtered from the resulting diethyltellurone. It melts at 98°, and loses iodine in the air, regenerating the α-di-iodide. (After reduction with sulphur dioxide and addition of nitric acid, Volhard's method gave I, 71. $TeEt_2I_4$ requires I, 73·2%).

The β-di-iodide does not combine with iodine under the conditions described above.

Preparation and Properties of the α-Base.—The α-base, which was described by Mallet as a colourless, crystalline mass, and by Wöhler as a white, amorphous mass, was prepared by grinding the solid α-di-iodide with fresh moist silver oxide, in exactly the same way as the corresponding dimethyl base. When hydriodic acid was added to the aqueous solution, the α-di-iodide was regenerated as a bright yellow precipitate, settling to a red solid. Silver nitrate gave a white precipitate, turning brown and then black. On evaporation to dryness at 100° under 15 mm. pressure, a colourless oily residue was left, which changed to a white non-crystalline solid when it was allowed to cool and to come in contact with cold water. This product, which was sparingly soluble in water and insoluble in organic solvents, decolorised permanganate and liberated violet fumes of iodine when warmed with concentrated hydriodic acid. Analysis showed that the α-base had been oxidised to *diethyltellurone*, $TeEt_2O_2$ (0·0254 g. gave 0·0147 g. Te when oxidised with aqua regia and reduced with sulphur dioxide and hydrazine hydrochloride: Te, 58·0. $TeEt_2O_2$ requires Te, 58·6%).

Preparation and Properties of the β-Base.—The β-base was obtained by evaporating a solution of the α-base to dryness at 100° under 15 mm. pressure in a stream of nitrogen. In order to dissolve it, a sealed tube of air-free water was broken inside the flask, which was then filled with nitrogen under atmospheric pressure. The β-base was then quite stable and resistant to oxidation, but was mixed with some unchanged α-base and some diethyltellurone. To purify it, hydriodic acid was added to the solution, and the mixed di-iodides were washed with a few drops of cold chloroform (in which the α-di-iodide is freely soluble); the pure β-di-iodide was then reconverted into the β-base by the action of silver oxide.

The β-base gives a faint white precipitate with silver nitrate, which turns black on boiling, but not in the cold. With hydriodic acid it gives a dark red precipitate of the β-di-iodide which settles to a purple solid; the presence of any α-base as impurity can be

detected by the formation of a fine yellow precipitate which remains at the top of the beaker.

Preparation and Properties of the β-Di-iodide.—The *β-di-iodide* can be prepared in a crude form by the action of hydriodic acid on the crude β-base, and freed from the α-isomeride by washing with chloroform, in which it is almost insoluble. It can also be obtained (free from the α-isomeride) by the action of hydriodic acid on diethyltellurone. It separates from methyl alcohol in dark purple crystals, m. p. 42° (Found: I, 57·2. $TeEt_2I_2$ requires I, 57·9%). It is also readily soluble in acetone, but gives a lachrymatory vapour (possibly iodoacetone) when the solution is evaporated.

α- and β-Dibromides.—The α-dibromide was obtained by Wöhler as a pale yellow oil of high boiling point. We obtained it in a similar form (Found: Br, 46·2. Calc. for $TeEt_2Br_2$: Br, 46·4%), but found that it solidified when cooled with a freezing mixture of ice and salt. When freed from the mother-liquor and dried in a vacuum desiccator, the solid does not melt till + 24°, but it does not then resolidify on cooling. The *β-dibromide* was obtained as a yellow oil of deeper colour, and solidified to a glass at −12° (Found: Br, 46·0. $TeEt_2Br_2$ requires Br, 46·4%).

α- and β-Dichlorides.—The α-dichloride was prepared by Mallet, who distilled it without decomposition at a temperature too high to be measured. We obtained it as a colourless oil (Found: Cl, 27·0. Calc.: Cl, 27·6%) which froze to a glass in a freezing mixture at −12°, and melted again at −5°. The *β-dichloride* was also obtained as a colourless oil (Found: Cl, 27·8. $TeEt_2Cl_2$ requires Cl, 27·6%) which solidified in a freezing mixture and melted again at −10°.

Action of alkalis. (a) In order to prepare a "dioxyiodide," the α-di-iodide was ground up with a little concentrated ammonia, dissolved in the minimum quantity of water, and left to crystallise in a vacuum desiccator. Colourless crystals separated, which melted at 107° and turned red on exposure to air; but these were shown by analysis to be an *α-monoxyiodide*, to which the formula $I[TeEt_2{\cdot}O{\cdot}TeEt_2]I$ may be assigned (I, 39·0; calc., 39·5%). When the crystals were boiled with water and cooled, in order to convert the supposed "dioxyiodide" into a "monoxyiodide," the same product was obtained (I, 39·9; calc., 39·5%), but in a less pure form, since it melted at 104—106°. This was a sticky, orange-yellow precipitate, which resembled the yellow "monoxyiodide" of the methyl series; but, unlike the methyl compound, it did not lose its colour after long standing in contact with water; nor did it lose its colour when recrystallised from hot water.

(b) The product obtained by boiling the β-di-iodide with half an

equivalent of sodium carbonate in concentrated solution, and then cooling, was a white precipitate, which was washed with a drop of ice-cold water. It had the properties of a *triethyltelluronium iodide*, since it did not change colour when exposed to acid fumes, and blackened without melting above 180°. It was appreciably soluble in water, but insoluble in organic solvents; it was therefore not easy to free it completely from sodium carbonate, the low percentage of iodine found on analysis thus being accounted for (Found: I, 35·9. $TeEt_3I$ requires I, 37·3%).

Action of mercury diphenyl. Vernon directs attention to the "almost unique" action of mercury diphenyl on α-dimethyltelluronium di-iodide and states that the interaction with the α-diethyl compound "does not take place in this curious manner." On mixing equimolecular solutions in chloroform of mercury diphenyl and of the α-di-iodide, $TeEt_2I_2$, the brown colour of the solutions became yellow, and after about 5 seconds a yellow precipitate was suddenly formed, very much as in the case of the dimethyl compound. This precipitate was a heavy, yellowish-green oil; when cooled to −8°, it solidified to a pale yellow, crystalline mass, and then remained solid up to 94°. (The α-methyl compound melts at 125°.) The addition compound is soluble in acetone, but does not crystallise well from this solvent. When boiled with chloroform or alcohol, it liberates a smell resembling that of carbylamine. Analysis showed that it contains two molecules of the di-iodide to one of mercury diphenyl [Found: Hg + Te, 36·3. $(TeEt_2I_2)_2,HgPh_2$ requires Hg + Te, 35·0%]. Mercury di-*p*-tolyl does not appear to interact with α-dimethyl- or α-diethyl-telluronium di-iodide.

Absorption Spectra.

The absorption spectra of the dimethyl series had been determined in specially dried alcohol in order to avoid hydrolysis (this vol., p. 308), but since Batley (*Trans. Faraday Soc.*, 1928, **24**, 438) has described a reaction between alcohol and iodine, it was thought preferable to measure the absorption spectra in a more inert solvent. They were therefore observed in *cyclo*hexane, which had been shaken with oleum and with sodium carbonate, dried, and fractionated.

The α-dihalides are readily soluble in *cyclo*hexane. The β-dihalides are only very sparingly soluble, but since only very dilute solutions were required, the concentrations of the saturated solutions were found to be sufficient. The extinction coefficients of the α- and β-di-iodides and of the α- and β-dibromides of the diethyl series were measured; but not those of the dichlorides or of the hydroxy-salts, which give only general absorption. For the

purpose of comparison, the absorption spectra of α- and β-dimethyltelluronium di-iodides were also measured in *cyclo*hexane.

The most important values of λ and of log ε are set out in Table I, and the corresponding absorption curves are plotted in Fig. 1. The general results are very similar to those already recorded for solutions of the dimethyl salts in alcohol, but the absolute values of the extinction coefficients in *cyclo*hexane are higher than in ethyl alcohol; the wave-length of the head of the band is also shorter in every case.

FIG. 1.

Molecular extinction coefficients in cyclo*hexane.*

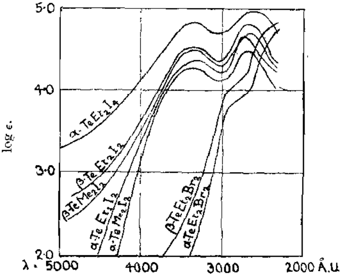


TABLE I.

Extinction Coefficients of Diethyltelluronium Dihalides.

α-$TeMe_2I_2$ λ = 3400 at log ε = 4·27; λ = 2680 at log ε = 4·47
β-$TeMe_2I_2$ λ = 3360 at log ε = 4·49; λ = 2640 at log ε = 4·70
α-$TeEt_2I_2$ λ = 3350 at log ε = 4·36; λ = 2700 at log ε = 4·65
β-$TeEt_2I_2$ λ = 3350 at log ε = 4·51; λ = 2670 at log ε = 4·80
α-$TeEt_2I_4$ λ = 3350 at log ε = 4·82; λ = 2630 at log ε = 4·95
α-$TeEt_2Br_2$ Step-out from λ 2900 to 2660 at log ε = 3·8 to 4·0
β-$TeEt_2Br_2$ Step-out from λ 2900 to 2690 at log ε = 4·0 to 4·2

Molecular Conductivities.

These were determined at 25° in cells of which the constants were 0·2240 and 0·1250 cm.$^{-1}$. Since the dihalides were difficult to dissolve and it was inadvisable to boil them with water, they were dissolved in the minimum quantity of cold ethyl alcohol and the solutions were diluted with cold conductivity water. The amount of alcohol in the most concentrated solution is shown in parentheses in Table II and was never more than 4%; and this, of course, is halved at each dilution. A correction, of 2½ times the percentage of alcohol, was applied to the final conductivity values. The

validity of this correction has already been demonstrated (thi vol., p. 313).

The solutions of the bases were standardised by titration agains N/10-hydrochloric acid with bromophenol-blue as indicator. Solu tions of the hydroxyhalides were prepared by mixing equimolecula solutions of dihalide and base. The β-dichloride was not inves tigated, since after purification and analysis there was not sufficien material available.

The molecular conductivities at 25° are summarised in Table II The behaviour of the salts is similar to that of the dimethyl salts but there is some contrast in the behaviour of the bases. Fo instance, whilst the α-base has the same low conductivity as the corresponding methyl base, the β-base has a conductivity ranging from 8 to 16 units as compared with 34 to 37 for the β-base of the methyl series. The somewhat higher values recorded for the β-base prepared from α-base are doubtless due to traces of impurities in the solution. A solution of the crystalline oxyiodide $I[TeEt_2{\cdot}O{\cdot}TeEt_2]I$, made up without the use of alcohol, gave molecular conductivities which were slightly less than twice the values recorded for the hydroxyiodide, exactly as was observed in the methyl series (this vol., p. 2006).

TABLE II.

Molecular Conductivities of Diethyltelluronium Compounds at 25°

(*Corrected for alcohol content.*)

v =	256.	512.	1024.	2048.	4096.
(a) *Dihalides.*					
α-$TeEt_2Cl_2$ (1·5) *	505	514	520	524	529
α-$TeEt_2Br_2$ (3)	503	511	517	521	523
α-$TeEt_2I_2$ (4)	504	512	518	524	527
α-$TeEt_2I_4$ (4)	—	493	499	501	503
β-$TeEt_2Br_2$ (1·8)	507	514	521	527	528
β-$TeEt_2I_2$ (4)	506	512	517	524	529
(b) *Hydroxy-halides.*					
α-$TeEt_2(OH)Cl$ (0·3)	97	104	108	110	113
α-$TeEt_2(OH)Br$ (0·8)	100	104	107	109	114
α-$TeEt_2(OH)I$ (1·5)	98	100·5	102	107	111
α-$(TeEt_2)_2OI_2$ (0)	185	194	198	204	213
β-$TeEt_2(OH)Br$ (1)	104	104·5	106·5	110	112
β-$TeEt_2(OH)I$ (2)	99·5	102	104·5	107	109

v =	32.	64.	128.	256.	512.	1024.
(c) *Bases.*						
α-$TeEt_2(OH)_2$	2·7	3·3	3·9	4·55	5·85	8·0
β-$TeEt_2(OH)_2$						
from α-base	10·5	11·4	12·6	13·5	15·1	—
from β-salt	8·6	9·5	10·5	12·8	—	—

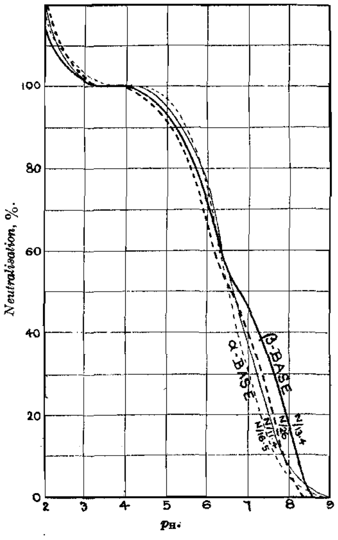
* The numbers in parentheses show the percentage of alcohol in the most concentrated solution.

Potentiometric Titrations.

These were carried out with a glass electrode, *N*-hydrochloric acid being used for the titration. The glass electrode had a very thin bulh, and gave about 56 millivolts per p_H. The potentials were checked by taking readings of an acid and an alkaline solution of

FIG. 2.

Potentiometric titrations.



nown p_H every time a titration was made. Two curves for the -diethyltelluronium base and two for the β-base (prepared in each ase from the β-salt) are shown in Fig. 2, and some of the principal ata are summarised in Table III.

The curves for the α-base are quite normal; those for the β-base ow an intermediate inflexion at 50% neutralisation, although of a ss pronounced character than in the case of the methyl base. The iflexion at 100% neutralisation corresponds in each case with the

ormation of the hydroxyhalide, $[TeEt_2OH]Cl$, but there is no sign of the second hydroxyl being neutralised at 200% neutralisation, nor is there any indication of basic compounds apart from the inflexion in the curves for the β-base. The curve for the $N/16{\cdot}5$-solution of the α-base is on the acid side of that for the $N/11{\cdot}4$-solution, as might be expected; this is also true of the $N/26$- and $N/13{\cdot}4$-solutions of the β-base. An anomaly is found in the fact that the foot of the curve for the α-base is on the alkaline side of that for the β-base, which has a higher molecular conductivity; but we do not attach any importance to this anomaly, since it disappears after 2 or 3 drops of acid have been added.

The data cited in Table III show that the dissociation constant K_b of the α-base is given by $-\log K_b = 7{\cdot}5$. The strength of the β-base cannot be deduced from the p_H at half-neutralisation, since the curve is inflected at this point, but it can be deduced fro the relation $-\log K_b = \log\{(1-x)/x\} + p_{K_w} - p_H$, where x the fraction of base neutralised. The p_H at 25% neutralisatic then gives $-\log K_b = 6{\cdot}7$. The β-base is therefore stronger tha the α-base, which is in accordance with the conductivity measur ments. The p_H at 75% neutralisation shows that the dissociatio constant of the basic salt formed at 50% neutralisation of th β-base is $-\log K_b = 7{\cdot}62$.

The relationship between the dimethyl- and the diethyl-telluro ium bases is as follows: the two α-bases are of exactly the sam strength, $-\log K_b = 7{\cdot}5$; the true β-methyl base, $-\log K_b = 6{\cdot}$ is stronger than the β-ethyl base, $-\log K_b = 6{\cdot}7$; but the bas salt $2TeEt_2O,HCl$, $-\log K_b = 7{\cdot}62$, is a stronger base than th basic salt $2TeMe_2O,HCl$, $-\log K_b = 8{\cdot}7$.

TABLE III.

Potentiometric Titrations.

Neutralisation.		p_H. Initial.	50%.	100%.	98%.	102%.	Range of p_H 98% to 102%.
α-Base	$N/16{\cdot}5$	8·90	6·5	3·8	4·88	3·14	1·74
α-Base	$N/11{\cdot}4$	9·08	6·55	3·8	4·72	2·86	1·86
β-Base	$N/26{\cdot}0$	8·30	6·60	3·64	4·30	3·00	1·30
β-Base	$N/13{\cdot}4$	8·60	6·78	3·63	4·48	2·86	1·62

Summary.

1. α-Diethyltelluronium di-iodide yields an α-base, which i converted into an isomeric β-base when the aqueous solution i evaporated to dryness in a vacuum.

2. From the β-base a series of β-salts can be prepared. The tw series of salts differ in their behaviour towards alkali, since th

α-iodide gives a colourless monoxyiodide, whereas the β-iodide gives a triethyltelluronium salt; and a tetra-iodide could only be prepared from the α-base.

3. The β-base is stronger than the α-base, and gives an inflected potentiometric curve, as in the methyl series.

We are indebted to the Department of Scientific and Industrial Research for a maintenance grant to one of us (F. L. G.) during the period in which this research was made.

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CAMBRIDGE. [*Received, October 31st, 1928.*]

CCCCXXII.—*Stereoisomerism of Disulphoxides and Related Substances. Part III. Some Pairs of Aromatic Disulphoxides.*

By ERNEST VERE BELL and GEORGE MACDONALD BENNETT.

AN examination of the products of oxidation of several aromatic disulphides of the general formulæ $Ar{\cdot}S{\cdot}C_2H_4{\cdot}SAr$ and $C_6H_4(SR)_2$ shows that in each case a pair of diastereoisomeric disulphoxides is produced.

s-Dibenzylthiolethane was oxidised by Fromm, Benzinger, and Schäfer (*Annalen*, 1912, **394**, 325) to a disulphoxide of m. p. 198°. A re-investigation of this substance shows it to be a mixture of two *isomerides* melting at 209° and 191° respectively. We have also prepared two new disulphides of the same type, namely, *s-diphenylthiolethane*, m. p. 69°, and *s-di-*p*-tolylthiolethane*, m. p. 81°, and each was oxidised by hydrogen peroxide to a mixture in about equal proportion of two isomerides: the *ethylene diphenyl disulphoxides*, α- of m. p. 166° and β- m. p. 123°; the *ethylene di-*p*-tolyl disulphoxides*, α- m. p. 174° and β- m. p. 127°.

The oxidation of *m*-dimethylthiolbenzene yields an α-*disulphoxide*, m. p. 147°, and a β-*disulphoxide*, m. p. 102°, each distinct in properties from the substance described by Zincke and Krüger (*Ber.*, 1912, **45**, 3468), which was doubtless a mixture of the two. The α-disulphoxide, m. p. 133°, of *m*-dibenzylthiolbenzene is, however, evidently identical with the disulphoxide obtained by the same authors, but we have isolated in addition a β-*disulphoxide*, m. p. 123°, from the mother-liquors of crystallisation of the former substance.

In the same way, the disulphoxide, m. p. 188°, (now α-) of *p*-dimethylthiolbenzene (Zincke and Frohneberg, *Ber.*, 1909, **42**, 2721) was found to be accompanied by a more soluble β-*disulphoxide*,

m. p. 136°, which, like its isomeride, yields a crystalline *mercuri-chloride*.

The members of each of these pairs of isomerides are sharply differentiated by their melting points, crystal forms and solubilities. In each case they were shown to be readily reduced to the parent disulphide, the alternative structure of a monosulphone being thereby excluded. Mixtures of the two related substances do not show a sharply depressed melting point, but in all cases melt ovei a range of temperature.

Negative results were obtained when attempts were made tc isolate a crystalline bromide or hydrochloride of any of thes disulphoxides (compare Part II, this vol., p. 86).

EXPERIMENTAL.

Condensation of Thiophenol and p-*Thiocresol with Ethylene Di bromide*.—Thiophenol (13·5 g.) in ethyl alcohol (100 c.c.) was heate on the steam-bath for 1 hour with potassium hydroxide (6·9 g. in little water) and ethylene dibromide (11·3 g.). When the solven had been removed in a current of steam, the residual oil solidifie on cooling (yield, 14·6 g.). s-*Diphenylthiolethane*, thus obtaine crystallised from ethyl alcohol in colourless, monoclinic plates, m. 69° (Found: C, 68·0; H, 5·8. $C_{14}H_{14}S_2$ requires C, 68·3; H, 5·7%

A similar operation using *p*-thiocresol (31·0 g.) gave s-*di-tolylthiolethane* (30 g.), which crystallised from ethyl alcohol colourless, monoclinic plates, m. p. 81° (Found: S, 23·4. $C_{16}H_{18}$ requires S, 23·35%).

Oxidation of the Disulphides with Hydrogen Peroxide.—In all cas to be described in this paper, the disulphide was oxidised by addi to its solution in glacial acetic acid the calculated amount of 25 hydrogen peroxide. After 24 hours the acetic acid was removed fr the mixture in a current of steam, followed by evaporation dryness on a steam-bath, the crude oxidation product being tl obtained in quantitative yield.

Isomeric Dioxides from Diphenylthiolethane.—The crude oxidat product, insoluble in water, but soluble in most organic solver was separated, by fractional crystallisation from toluene, into t isomerides which appear to be formed in approximately eq proportion.

The *α-disulphoxide* (yield of pure substance from 5 g. of disulphoxide, 1·2 g.) formed colourless, monoclinic plates or tal m. p. 166° (decomp.), from ethyl alcohol (Found: C, 60·3; H, S, 23·3. $C_{14}H_{14}O_2S_2$ requires C, 60·4; H, 5·0; S, 23·0%). *β-disulphoxide* (yield, 0·8 g.) separated from alcohol in colou needles with straight extinction, m. p. 123° (decomp.), and

much more soluble in organic solvents than the preceding substance (Found : S, 22·8%).

Reduction of the Disulphoxides.—In this and each other instance the isomerides were reduced in alcoholic solution by means of zinc dust and hydrochloric acid and the product was found by its melting point and by that of a mixture with the parent disulphide to be identical with the latter.

*Isomeric Dioxides of Di-*p*-tolylthiolethane.*—The oxidation product was a mixture of two substances, present in equal proportion and separated by fractional crystallisation from toluene. The *α-disulphoxide* (yield of pure substance, 1·1 g. from 9·1 g. of disulphide) may be crystallised from benzene, toluene, xylene, ethyl, butyl or amyl alcohol, or ethyl acetate, but it is insoluble in water. It separates from ethyl alcohol in small rhomb-shaped plates with diagonal extinction and a high double refraction; m. p. 173—174° (decomp.) (Found : S, 20·8. $C_{16}H_{18}O_2S_2$ requires S, 20·9%). The *β-disulphoxide* (yield, 0·9 g.) is more soluble in all solvents than its isomeride, but is insoluble in water. It separates from its highly concentrated solution in ethyl alcohol in needles with straight extinction, m. p. 126—127° (decomp.) (Found : S, 20·7%).

Isomeric Dioxides of Dibenzylthiolethane.—The crude dioxides (10·7 g. from 10·0 g. of the disulphide) were separated by crystallisation from amyl alcohol. The *α-disulphoxide* separated in small monoclinic plates from ethyl or amyl alcohol or 50% acetic acid, and in flat prisms from xylene, m. p. 209° (Found : S, 21·0. $C_{16}H_{18}O_2S_2$ requires S, 20·9%). The *β-disulphoxide* was freed from the last traces of the α-isomeride by crystallisation from xylene. It separated from xylene or amyl alcohol in feathery needles having a straight extinction, m. p. 192° (Found : S, 21·0%). The disulphoxide described by Fromm, Benzinger, and Schäfer (*loc. cit.*) had m. p. 198°.

Isomeric Dioxides of 1 : 3-*Dimethylthiolbenzene.*—The crude product of oxidation was separated by crystallisation from benzene into two substances present in approximately equal quantities : the *α-disulphoxide*, crystallising from benzene in plates with a high double refraction and a straight extinction, m. p. 147° (Found : S, 32·0. $C_8H_{10}O_2S_2$ requires S, 31·7%), and the more soluble *β-disulphoxide*, which separated from benzene in rhomb-shaped crystals with an oblique extinction, m. p. 102° (Found : S, 31·8%). The substance described by Zincke and Krüger (*loc. cit.*) had m. p. 131°.

The reduction of these two disulphoxides yielded the parent disulphide, which is a liquid. Its identity was confirmed in both cases by the preparation of the crystalline *mercurichloride* of 1 : 3-

dimethylthiolbenzene, m. p. 108° (Found : Hg, 45·5. $C_8H_{10}S_2Cl_2Hg$ requires Hg, 45·3%).

Isomeric Dioxides of 1 : 3-*Dibenzylthiolbenzene*.—Two substances, present in about equal proportion, were separated from the oxidation product by fractional crystallisation from toluene and mixtures of this solvent with petroleum of b. p. 100—120°.

The α-*disulphoxide* crystallised from toluene or ethyl alcohol in almost square plates with diagonal extinction, m. p. 133° (Found : S, 18·0. $C_{20}H_{18}O_2S_2$ requires S, 18·1%). The more soluble β-*disulphoxide* separated in minute, rhomb- or hexagonal-shaped crystals from toluene and in characteristic spherical aggregates from carbon tetrachloride; m. p. 123° (Found : S, 18·3%). The substance described by Zincke and Krüger had m. p. 131°.

Isomeric Dioxides from 1 : 4-*Dimethylthiolbenzene*.—The crude mixture was readily soluble in water and moderately easily soluble in other solvents. Crystallisation from toluene, ethyl alcohol, benzene, and ethyl acetate separated two isomeric dioxides. The α-disulphoxide (yield, 2·3 g. of pure substance from 10 g. of the disulphide) crystallised from water in rhomb-shaped plates with an oblique extinction, m. p. 183° (Found : S, 31·7. Calc. for $C_8H_{10}O_2S_2$: S, 31·7%). Zincke and Frohneberg (*loc. cit.*) gave the m. p. as 188°. The mercurichloride was obtained in silvery plates, m. p. 216° (decomp.), sparingly soluble in water (Found : Hg, 42·25. Calc. for $C_8H_{10}O_2Cl_2S_2Hg$: Hg, 42·3%). Zincke and Frohneberg give the m. p. as 220°. The β-*disulphoxide* (yield, 2·2 g.) is more soluble than its isomeride in all solvents. It crystallises in branching needles with an oblique extinction, m. p. 136° (Found : S, 31·7%), and forms a mercurichloride similar to that of the α-isomeride, but much more readily soluble in water and having m. p. 188° (decomp.).

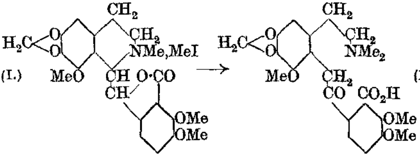
Note on the Determination of Sulphur.—The method of Pregl ("Quantitative Organic Microanalysis," English ed., 1924, p. 102) has proved very useful on the *macro*-scale. Ordinary combustion tube is constricted at a point which divides it into a length of 50 cm. (for the boat and platinum catalysts) and 35 cm. (for glass beads). The acid produced is titrated with *N*/10-alkali and phenolphthalein. The time required for an analysis is less than for an ordinary combustion.

THE UNIVERSITY, SHEFFIELD. [*Received, November 1st*, 1928.]

CCCCXXIII.—*Degradation of Quaternary Ammonium Salts. Part I.*

By Thomas Stevens Stevens, Elton Marshall Creighton, Alexander Brown Gordon, and Malcolm MacNicol.

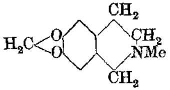
In the course of synthetic work a method was required whereby the nitrogen atom of a secondary amine might be protected in such a way as to admit of quaternary salt formation and subsequent removal of the protecting group : the most obvious solution was the insertion of an alkyl radical which should be removed with special ease in a Hofmann degradation of the subsequently formed quaternary salt. Now quaternary salts derived from tetrahydro*iso*quinoline readily undergo such degradation with rupture of the bond between the nitrogen atom and carbon atom 3, but the conversion of narcotine methiodide (I) into narceïne (II) forms a notable exception. This fact suggested that the group Ph·CH(OH)·CH_2· might prove suitable.

(I.)  (II.)

Preliminary experiments showed that styrene iodohydrin did not readily yield quaternary salts, and accordingly salts were prepared from ω-bromoacetophenone and tertiary bases, and submitted to reduction with sodium amalgam. It is probable, however, that the removal of the phenacyl group under these conditions is not due to its reduction to β-hydroxy-β-phenylethyl and subsequent Hofmann degradation, for it was found that *phenacylbenzyldimethylammonium bromide* yielded benzyldimethylamine on reduction in *acid* solution, and similar observations have been recorded by Schmidt and Rumpel (*Arch. Pharm.*, 1899, **237**, 222) and by Emde and Runne (*ibid.*, 1911, **249**, 354). Emde's systematic study of the reduction of ammonium salts has shown that of the commonly occurring radicals benzyl is most loosely held, but it was necessary for the present purpose to find a still more easily detachable group.

The phenacylo-bromides or -iodides of β-phenylethyldimethylamine, dimethylpiperazine, hydrohydrastinine (III), benzyldimethylamine, and α-phenylethyldimethylamine were investigated;

the *first three salts readily lost the phenacyl group on reduction* with sodium amalgam, but the last two reacted abnormally (*vide*



(III.)

infra). The results show that the removal of the phenacyl group by reduction may leave intact structures which exhibit little stability towards other methods of degradation. The satisfactory results obtained with the salt derived from dimethylpiperazine are of particular interest, since the piperazine ring is opened with exceptional ease by Hofmann degradation (von Braun, Goll, and Zobel, *Ber.*, 1926, **59**, 936).

When an aqueous solution of phenacylbenzyldimethylammonium bromide (IV) is treated with sodium amalgam, the reaction does not proceed normally with elimination of the phenacyl radical, but yields a solid base, $C_{17}H_{19}ON$, which is also produced in excellent yield by heating the salt (IV) with dilute sodium hydroxide solution. The analytical data are not inconsistent with the formula $C_{16}H_{17}ON$ (= $Ph{\cdot}CO{\cdot}CH_2{\cdot}NMe{\cdot}CH_2Ph$), but the degradation has not takei the unusual course of removing a methyl group preferentially t benzyl or phenacyl, since the *methobromide* of the new base is no identical with the salt (IV). Hot alkali converts this methobromid into phenyl styryl ketone, so that the solid base would appear t have the constitution (V) or (VI). The former alternative i favoured, and the presence of an $\alpha\gamma$-diphenylpropane skeleto confirmed, by the observation that the methobromide yields benzy acetophenone on reduction.

(IV.) $Ph{\cdot}CO{\cdot}CH_2{\cdot}NMe_2Br{\cdot}CH_2Ph$ $\qquad$ $Ph{\cdot}CO{\cdot}CH_2{\cdot}CH(NMe_2)Ph$ (VI.

(V.) $Ph{\cdot}CO{\cdot}CH(NMe_2){\cdot}CH_2Ph$ $\qquad$ $Ph{\cdot}CO{\cdot}CHBr{\cdot}CH_2Ph$ (VI

The formula (V) was shown by synthesis to be the correct on Benzylacetophenone yields the substance (VII) on bromination, tl position of the bromine atom being confirmed by the non-identi of the compound with the known β-bromobenzylacetopheno (Rupe and Schneider, *Ber.*, 1895, **28**, 958; Vorländer and Tuban *Ber.*, 1904, **37**, 1652). By the action of dimethylamine, (VII) yiel a product identical with the base $C_{17}H_{19}ON$. The synthesis mig conceivably give rise to the isomeride (VI) by removal of hydrog bromide from (VII), followed by addition of dimethylamine to t unsaturated ketone, but experiments on the addition of dimeth amine to phenyl styryl ketone have yielded only small quantit

of very unstable basic material, in general agreement with the observation of Georgi and Schwyzer (*J. pr. Chem.*, 1912, **86**, 273) that β-piperidinobenzylacetophenone is highly unstable.

Phenacyl-α-phenylethyldimethylammonium iodide yields with alkali a presumably similar solid base which will be described in a future communication.

This peculiar migration of the benzyl radical is probably due to the combined effect of the relative toleration of the benzyl group for a positive charge (compare Hanhart and Ingold, J., 1927, 1003) and the reactivity of the methylene group in the phenacyl radical, but we prefer not to speculate further as to the mechanism of the reaction until more experimental data are forthcoming.

The fact that the substance (I) yields benzyldimethylamine on reduction in acid solution shows that the quaternary salt has the structure assigned to it, and that the migration takes place during the treatment with alkali.

EXPERIMENTAL.

The following tertiary bases were prepared according to the references quoted: β-phenylethyldimethylamine (Decker and Becker, *Ber.*, 1912, **45**, 2404), dimethylpiperazine (Eschweiler, D.R.-P. 80520, 1893; Knorr, Hörlein, and Roth, *Ber.*, 1905, **38**, 3136), benzyldimethylamine (Eschweiler, *loc. cit.*; Sommelet and Guioth, *Compt. rend.*, 1922, **174**, 687). The quaternary salts were obtained by refluxing the base (1 mol.) with bromoacetophenone (1 mol.) in benzene solution for ½—1 hour, except in the case of that derived from diethylaniline, the reaction here being carried out in hot alcohol or cold acetone. The bromide was either recrystallised from alcohol–ether, or converted by potassium iodide solution into the iodide, and the latter purified in like manner. Reduction of the salts was carried out in hot aqueous solution by an excess of sodium amalgam.

Phenacylphenyldiethylammonium iodide forms a microcrystalline powder, m. p. 133° (Found: I, 32·5. $C_{18}H_{22}ONI$ requires I, 32·2%). The preparation of this and other quaternary salts containing the nitrogen atom directly attached to an aromatic nucleus did not proceed smoothly (compare Wedekind, *Ber.*, 1908, **41**, 2802), and their degradation appeared to take an abnormal course, which is under investigation.

Phenacyl-β-phenylethyldimethylammonium bromide forms clusters of minute prisms, m. p. 191° (Found: Br, 23·2. $C_{18}H_{12}ONBr$ requires Br, 23·0%). After degradation, the β-phenylethyldimethylamine was identified as picrate and as methiodide (Decker and Becker, *loc. cit.*).

Diphenacyldimethylpiperazinium dibromide is rather sparingly soluble in water or alcohol, and crystallises from these solvents in small laminæ, m. p. 222—225° (decomp.) (Found : Br, 30·8. $C_{22}H_{28}O_2N_2Br_2$ requires Br, 31·2%). The salt appeared to be homogeneous, but no very thorough search was made for the second theoretically possible stereoisomeride. After reduction, the regenerated dimethylpiperazine was distilled in steam and isolated as the very sparingly soluble picrate (decomp. 280°) (Knorr, Hörlein, and Roth, *loc. cit.*). It was further characterised by the red precipitate produced with potassium bismuth iodide, and by reconversion, through the hydrochloride, into the original phenacylobromide.

Hydrohydrastinine phenacyloiodide separates from water or alcohol, in both of which it is sparingly soluble, in spherical aggregates of minute prisms, m. p. 190° (Found : I, 28·9. $C_{19}H_{20}O_3NI$ requires I, 29·1%). From the liquors after reduction, benzene extracted hydrohydrastinine, m. p. and mixed m. p. 64°.

Phenacylbenzyldimethylammonium bromide forms small prisms, m. p. 167—168° (Found : Br, 24·2. $C_{17}H_{20}ONBr$ requires Br, 24·0%). Reduction with zinc dust and sulphuric acid gave a steam-volatile base whose methiodide underwent partial fusion at 170° (m. p. of benzyltrimethylammonium iodide, 177—178°), but was not completely melted below 250°. With picric acid, however, the iodide yielded benzyltrimethylammonium picrate, m. p. and mixed m. p. 173—174° (Goss, Hanhart, and Ingold, J., 1927, 259, give 168—169°); the crude iodide probably contained phenacyltrimethylammonium iodide, or the tetramethylammonium salt produced from the latter by the action of excess of methyl iodide.

ω-Dimethylamino-ω-benzylacetophenone (V).—(*a*) Phenacylbenzyldimethylammonium bromide is heated on the water-bath with excess of 10% sodium hydroxide solution for 1 hour. The oily product solidifies on cooling and is recrystallised from aqueous methyl alcohol. Yield, 90%. (*b*) ω-Bromo-ω-benzylacetophenone (*vide infra*) (1 mol.), dimethylamine hydrochloride (2 mols.), and sodium methoxide (2 mols.) are mixed in methyl-alcoholic solution kept over-night, and warmed for 2 hours on the water-bath. The diluted mixture is extracted with benzene and the product is extracted from the benzene by hydrochloric acid and precipitated by ammonia.

ω-Dimethylamino-ω-benzylacetophenone forms colourless leaflets m. p. 77—79°, which are moderately easily soluble in methyl alcohol and readily soluble in benzene or light petroleum (Found : C, 80·7 80·8; H, 7·4, 7·4; *M*, cryoscopic in benzene, 252. $C_{17}H_{19}ON$ requires C, 80·6; H, 7·5%; *M*, 253). The substance is slightly volatile in steam and slowly resinifies on keeping. It does not

appear to react with hydroxylamine, semicarbazide, or *p*-nitrophenylhydrazine, and is comparatively stable towards acid permanganate. The *picrate* crystallises from alcohol in bright yellow swordblades, m. p. 147—149° (Found : N, 11·8. $C_{17}H_{10}ON,C_6H_3O_7N_3$ requires N, 11·6%). The identity of the products yielded by methods (*a*) and (*b*) was shown by direct comparison and mixed melting points of the base and of the picrate.

The methosulphate, prepared in benzene solution, yields the *methobromide* on addition of potassium bromide to its solution in water. This salt separates from alcohol–ether in faintly pink prisms, m. p. 195—197° (Found : Br, 21·9, 21·4; loss at 130°, 6·2. $C_{18}H_{22}ONBr,\frac{1}{2}C_2H_6O$ requires Br, 21·6; loss, 6·2%). On heating on the water-bath with dilute sodium hydroxide solution it yields phenyl styryl ketone, identified as the α-dibromide (Pond, York, and Moore, *J. Amer. Chem. Soc.*, 1901, **23**, 790), m. p. and mixed m. p. 157°. By reduction with zinc dust and sulphuric acid, the methobromide yields benzylacetophenone, which was characterised by conversion into the semicarbazone (most readily purified from ether–light petroleum), m. p. and mixed m. p. 143° (Jacobson and Ghosh, J., 1915, **107**, 962).

ω-Bromo-ω-benzylacetophenone (VII) is obtained by the action of the theoretical quantity of bromine on benzylacetophenone in carbon tetrachloride. The reaction proceeds rapidly, and after the hydrogen bromide has been removed by a current of dry air the solvent is evaporated and the residue recrystallised from methyl alcohol. It forms minute prisms, m. p. 57—59° (Found : Br, 27·8. $C_{15}H_{13}OBr$ requires Br, 27·7%); the m. p. is depressed by admixture with β-bromobenzylacetophenone, prepared by the method of Vorländer and Tubandt (*loc. cit.*). The substance (IV) appears to show the acidic properties associated with α-halogeno-ketones in that it yields a golden-yellow solution with aqueous-alcoholic alkali.

THE UNIVERSITY, GLASGOW. [*Received, October 27th, 1928.*]

CCCCXXIV.—*Studies in the Composition of Coal. The Active-decomposition Point of Coal.*

By RONALD HOLROYD and RICHARD VERNON WHEELER.

DURING the slow distillation of a bituminous coal in a vacuum, gases and liquids (water and oils) are evolved at quite low temperatures. At 100°, for example, traces of liquid pentane can be detected in the water which, together with "occluded" gases, may

be evolved in considerable quantity from an air-dried coal at that temperature. Such gases and liquids are not products of decomposition of the coal. Even the red oils that first make their appearance at about 225° are not decomposition products, but are liquated *from the coal conglomerate, being yielded by free hydrocarbons.* The main mass of the coal begins to decompose at a definite temperature which, for a given coal under standard conditions of heating, is constant within $\pm 2°$. Wide variations in the experimental conditions do not markedly affect the result, but this temperature of active decomposition varies for different coals. Representing *as it does the beginning of disruption by heat of the ulmin* molecules, it would appear to be an important constant characteristic of the type and properties of different coals, and we have therefore determined it for a number of samples.

Before recording the results, we must recount the observations, referred to briefly in our paper on oil-yielding constituents (this vol., p. 2669), which enable this decomposition point to be specified and related to the *ulmin constituents* of the coal.

The method of experiment involved the heating of 250-g. charges of the finely powdered coals under high vacuum at different temperatures, the standard period of heating at each temperature being 120 hours. Under these conditions, the action of heat on the individual ingredients of the coal could be followed comparatively easily. *No marked decomposition occurred* with any bituminous coal below about 300°: as recorded in our previous paper, for example, Wigan Six Foot coal first began to decompose rapidly over the range 315—320°.

The characteristic products of this extensive decomposition during its early stages are, with all coals, water, phenolic oils (yielded *exclusively by the ulmin constituents of the coals*, see J., 1915, **107**, 1318), and gaseous paraffins. Prolonged heating of a coal just below its decomposition point yields only small quantities of these characteristic products, whilst prolonged heating just above it yields greatly enhanced quantities. This is well illustrated by the results recorded in Table I. With the Wigan Six Foot coal, parallel distillations were carried out at 300° and 320° during 120 hours (the "standard" period of heating) and at 310° and 325° during 750 hours.

In Table I, the italicised figures in particular relate to the active-decomposition point. The high yields of oils on prolonged heating at 310°—higher yields than during the "standard" distillation at 320°—require explanation. For the most part, these are *not products of decomposition of the main mass of the coal*, but as will be demonstrated in another communication, are derived

TABLE I.

The Active Decomposition of Wigan Six Foot Coal. Gaseous and Liquid Products.

(Gaseous products in c.c. per 100 g. Liquid products as percentages on the ash-free, dry coal.)

	At 300°, 120 hrs.	At 310°, 750 hrs.	At 320°, 120 hrs.	At 325°, 750 hrs.
Total gas	178	279	602	1140
Carbon dioxide	66	94	134	190
Higher olefins	3·5	20	38	90
Ethylene	2·4	3·3	14·7	—
Carbon monoxide	14	35	40	—
Paraffins	*89*	*126*	*363*	*ca. 750*
Ratio C/A for paraffins	*1·05*	*1·16*	*1·51*	—
Water of decomposition	*0·29*	*0·35*	*0·79*	*1·52*
Total light oils	0·35	0·93	0·57	1·13
Total heavy oils	1·35	3·80	3·24	6·50
Phenolic oils	—	*0·26*	*0·37*	*0·95*
Saturated hydrocarbons	0·70	0·80	0·99	1·20
Unsaturated hydrocarbons	0·46	1·56	1·50	2·57
Oils soluble in ether and chloroform	0·13	0·57	0·17	1·30

from organised plant entities (mainly spore exines and cuticles), of which the Wigan Six Foot coal (mainly a clarain) contained about :%. Such, in particular, are the unsaturated hydrocarbons. The oils soluble in ether and chloroform were derived from resins, which began to decompose slowly at 310°, whereas during the "standard" distillations they began to distil (with partial decomposition) at 325—330°.

The solid residues remaining after the distillation of coals at different temperatures undergo marked changes in character when the active-decomposition point has been passed. The principal changes in the residues are summarised in Table II, the Wigan Six Foot coal again being taken as an example.

TABLE II.

The Active Decomposition of Wigan Six Foot Coal. Solid Products.

	Sol. in C_5H_5N. Insol. in $CHCl_3$. (% on ash-free, dry coal.)	Sol. in $CHCl_3$. Insol. in light petroleum and Et_2O. (% on ash-free, dry coal.)	Reactivity with oxygen (c.c. per g.).	Behaviour on coking.
Original coal	12·34	3·14	11·1	Swollen
Residue at 250°	8·79	1·93	—	Less swollen
Residue at 280°	8·12	1·67	7·4	Shrunken
Residue at 300°	8·25	1·51	6·4	Shrunken
Residue at 320°	10·08	2·95	7·0	Much swollen
Residue at 350°	5·73	1·02	6·4	Incoherent

The material "soluble in pyridine but insoluble in chloroform" termed β-compounds in the original coal, and regarded as ulmin

compounds that are dispersed rather than dissolved by pyridine) decreases in quantity in the residues obtained at temperatures below the decomposition point, but suddenly increases when that point has been passed. Similar remarks apply to the material soluble in chloroform but insoluble in light petroleum and ethyl ether. This material (termed γ_3- and γ_4-compounds in the original coal) behaves in some respects like the resins (see Cockram and Wheeler, J., 1927, 700), but in others, as this, like the ulmins. Simultaneously, therefore, with a marked evolution of gases and liquids, such as are known to be yielded on the break-down of the ulmin molecules, there is a marked change in the behaviour of the residues towards solvents, suggestive of a more comprehensive disruption than that of external groupings from the molecules. At lower temperatures, external groupings may be split off from the ulmin molecules, yielding water and the oxides of carbon (particularly from a partially oxidised coal), and causing a gradual decrease in reactivity.

Similarly, as the temperature of distillation was raised, the reactivity of the residues with oxygen gradually decreased, to increase suddenly as soon as the point of marked decomposition had been passed. The reactivity measurements recorded in Table II (made for us by Dr. A. L. Godbert) are expressed in terms of the volume of oxygen combining with the material at 150° under standard experimental conditions. They confirm observations, made by Graham and Coles (*Fuel*, 1928, **7**, 21), that the rate of oxidation of certain coals was considerably increased by preheating them in a vacuum at "critical" temperatures, between 300° and 400°, dependent on the character of the coals. These critical temperatures were, we conclude, the active-decomposition points of the coals. The compounds responsible for the reactivity of coal with oxygen have been shown by Francis and Wheeler (*Safety in Mines Research Board Paper* No. 28, 1926) to be the ulmin compounds.

Finally, the results of coking tests, carried out by heating in small crucibles at 900°, during 7½ minutes, 2-g. samples of the coals and residues from the distillations at different temperatures, revealed a marked change in this characteristic property of coal by preheating at the decomposition point, the coke produced from that residue being considerably more swollen than the coke from the original coal.

Such fundamental changes in the properties of the coal on being heated at a given temperature clearly mark the beginning of extensive molecular disruption. Francis and Wheeler (*loc. cit.*) conclude from their work that the nuclei of the ulmin molecules are compact systems of six-membered annular groupings connected together by

heterocyclic structures such as pyrrole and furan. Compounds having such structures might be expected to yield alkylised phenolic compounds and complex hydroaromatic hydrocarbons on decomposition (see Schrauth, *Brennstoff-Chem.*, 1923, **4**, 161). Such compounds have, in fact, been found to be characteristic decomposition products of the coal ulmins.

The Decomposition Points of Different Coals.

The active-decomposition points of a number of different coals, with data regarding the characteristic products of decomposition of most of them, have been determined. The results are summarised in Table III.

TABLE III.

Active-decomposition Points of Coals.

Description of coal.	Carbon content.*	Decomp. point.	Water of decomp., % (up to 400°).	Phenols and acids, % (up to 400°).
Seven Foot (Kingsbury)	77·0	290—300°	—	—
†Thick Seam, Brazills (Hamstead)	78·3	295—300	5·97	2·23
‡Ditto	80·9	(300)	5·40	1·36
†Barnsley (Brodsworth)	81·2	305—310	4·07	0·91
‡Ditto	82·7	(310)	4·08	0·85
Wigan Six Foot (Maypole)	82·8	315—320	4·09	1·94
Parkgate (Cadeby)	83·4	325—330	—	—
Silkstone (Rockingham)	83·7	325—330	1·82	0·83
Six-Quarter (Haig)	86·6	320—325	2·29	1·06
Busty (Tudhoe)	87·4	335—340	—	—
Busty (Beamish Mary)	88·4	340—345	—	—
Black Vein (Celynen)	88·5	340—345	1·51	0·56
Two Foot Nine (Ferndale No. 7)	89·8	360—365	0·81	0·06

* Calculated on the "pure coal" basis; see Table IV.
† Vitrain portion. ‡ Durain portion.

In the descriptions of the coals, the name of the seam is given first, with the name of the colliery or pit at which the seam was worked in parentheses. All the coals except those specified were clarains. With the two durains, the decomposition point could not be determined precisely, since there was incipient decomposition of a minor ingredient of the coal at a lower temperature. It will be seen that, in general, the decomposition point increased with the carbon content of the coal, a result to be expected if the decomposition is that of the ulmin constituents. There is a general tendency for the yields of water and phenolic compounds (expressed in Table III as percentages on the ash-free, dry coals) to be greater from the coals of lower carbon content. The yields of oxides of carbon above the decomposition point were also greater from the coals of lower carbon content.

In a paper entitled "The Primary Decomposition of Coal. I.

The Temperature of Initial Decomposition," *King* and *Willgress* (*Dept. Sci. Ind. Res., Fuel Res. Tech. Paper No.* 16, 1927) record results for three bituminous coals showing that, when they were heated in a stream of nitrogen, traces of oils were carried over at lower temperatures from the coals of higher carbon content, as follows: *C*, 74·5%, first appearance of oil at 245°; *C*, 83·87%, 230°; *C*, 85·43%, 215°. They say: "With bituminous coals the temperature of initial decomposition appears to increase with increasing oxygen content and decreasing carbon content." We are satisfied that the temperature at which oils first make their appearance when a bituminous coal is heated is not the temperature of initial decomposition of the coal, but that such oils are distilled unchanged. In our experience, the temperature at which such oils

TABLE IV.

Proximate and Ultimate Analyses.

Coal.	Proximate analysis. Moisture, %.	Ash, %.	Volatile matter, %, ash-free, dry.	Ultimate analysis, % on "pure coal" basis. C.	H.	N.	S.*	O.
Seven Foot	5·5	8·7	41·9	77·0	5·55	1·19	1·00	15·26
Thick Seam, vitrain	13·4	1·3	37·5	78·3	5·15	1·02	1·01	14·52
Thick Seam, durain	6·4	6·0	35·1	80·9	4·71	1·08	0·97	12·34
Barnsley, vitrain ...	6·4	1·3	33·0	81·2	5·31	1·34	1·03	11·12
Barnsley, durain ...	3·5	4·0	36·1	82·7	5·23	1·42	1·06	9·59
Wigan Six Foot ...	1·7	2·7	37·6	82·5	5·55	1·53	0·90	9·52
Parkgate	2·7	3·4	36·1	83·4	5·13	(Not determined)		
Silkstone	1·2	1·5	34·1	83·6	5·38	1·82	1·43	7·77
Six-Quarter	1·4	12·2	37·0	86·6	5·08	1·61	0·39	6·32
Busty (Tudhoe) ...	0·6	6·3	27·7	87·4	4·72	0·89	1·04	5·95
Busty (Beamish Mary)	0·8	7·9	28·7	88·3	5·27	1·58	0·57	4·28
Black Vein	0·9	6·8	30·8	88·5	5·02	1·53	0·83	4·12
Two Foot Nine	*0·6*	*5·6*	*16·7*	*89·8*	*4·18*	*1·39*	*0·88*	*3·75*

* Organic sulphur.

Rational Analyses, %.

Coal.	*Hydrocarbons and resins.*	*Organised plant entities.*	Ulmins.	*Reactivity index for ulmins.*
Seven Foot	—	2·8	—	76
Thick Seam, vitrain	3·2	Nil	96·8	74
Thick Seam, durain	3·5	7·8	88·7	72
Barnsley, vitrain	3·4	Nil	96·6	65
Barnsley, durain	2·7	20·7	76·6	62
Wigan Six Foot	3·0	4·1	92·9	50
Parkgate	4·8	2·0	93·2	61
Silkstone	3·6	4·0	92·4	52
Six-Quarter	4·0	7·2	88·8	55
Busty (Tudhoe)	4·3	7·4	88·3	45
Black Vein	—	6·6	—	39
Two Foot Nine	Trace	12·0	88·0	16

first appear bears no direct relation to the carbon content of the coal. It has, however, a tendency to be lower the greater the proportion of free hydrocarbons in the coal. Some decomposition of part of the coal substance undoubtedly occurs at a lower temperature than that specified as the "active-decomposition point." As already stated, the external groupings of the ulmin compounds may yield water and oxides of carbon in small amount at quite low temperatures (from about 150° upwards), whilst other parts of the coal conglomerate, such as the resins, spore exines, and cuticles, yield oils slowly at about 300°. Such decompositions do not materially affect the character of the coal, a loss of reactivity of the ulmin compounds being the most noticeable result. Marked changes of character only begin when the breakdown of the nuclear structure of the ulmin compounds begins.

Proximate, ultimate, and rational analyses of the coals referred to in this paper are given in Table IV. For the ultimate analyses, the usual calculations on an "ash-free, dry" basis have not been made; instead, allowance has been made for the fact that the mineral matter contained in a coal differs in composition and amount from the ash it yields on incineration. For the rational analyses, the methods described by Francis and Wheeler (this vol., p. 2967) were used.

NOTE.—Through an error in transcription, the figures in the first column of Table III of our previous paper (*loc. cit.*, p. 2675) were wrongly given. They should read: 81·54, 85·5, 86·1, 85·4, 79·0, 77·5.

The work described in this paper forms part of a research on the constitution of coal which we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish the results.

SAFETY IN MINES RESEARCH LABORATORIES,
SHEFFIELD. [*Received, October 23rd*, 1928.]

CCCCXXV.—*Explosions in Closed Cylinders. Part I. Methane–Air Explosions in a Long Cylinder. Part II. The Effect of the Length of the Cylinder.*

By WILLIAM ANTHONY KIRKBY and RICHARD VERNON WHEELER.

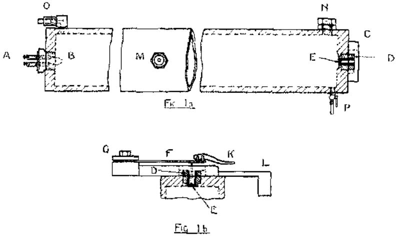
THE object of this research is the correlation of the movement of flame with the development of pressure during explosions in a closed cylinder the length of which is much greater than its diameter,

conditions which may be presumed to cause the movement of flame to differ considerably from that in a cylinder, the length and diameter of which are nearly equal, or in a sphere or cube, as in the experiments of Ellis and Wheeler (J., 1925, **127**, 764; 1927, 153).

Similar work has been carried out by Woodhury, Lewis, and Canby (*J. Soc. Automotive Eng.*, 1921, **8**, 209) with acetylene–air mixtures in a vertical cylinder 30·5 cm. long and 10·15 cm. in diameter. The mixtures were ignited at the base of the cylinder and simultaneous records were taken of the development of pressure and the movement of the flame as photographed through a window formed by a glass rod extending throughout the length of the cylinder. From the records it would appear that in each explosion the time of attainment of maximum pressure coincided with that

FIG. 1.

Explosion-cylinder and pressure gauge.



of the passage of flame through the mixture, whilst the time–pressure curves indicated arrests in the development of pressure simultaneous with arrests in the movement of the flame.

Morgan (*Proc. Inst. Auto. Eng.*, 1925, **15**, 27; *Phil. Mag.*, 1927, **3**, 1161) studied the development of pressure during explosions of coal-gas–air and methane–air mixtures in horizontal cylinders 4·45 cm. in diameter and either 30·5 or 61 cm. long, ignition being at one end. This work will be discussed more particularly in Part II, but the important point noted was the occurrence, under certain conditions, of strong and rapid vibrations at the crests of the time–pressure curves.

Method of Experiment.—The gun-metal cylinder (supported horizontally) is 200 cm. long and of 10 cm. internal diameter, its capacity being about 16 litres. Fig. 1*a* shows its two ends in cross-section and a side view of a portion of its length. At one end is an ignition plug, A, carrying platinum electrodes, B, projecting 1 cm.

into the cylinder and forming a spark-gap of 4 mm. The other end carries on a boss, C, a pressure recorder, shown in detail at Fig. 1*b*. The sleeve, D, of hardened steel, is screwed into the end of the cylinder, and the hollow piston, E, also of hardened steel, moves freely in it, being prevented from entering the cylinder by a thin collar. The movements of the piston under pressure developed by an explosion within the cylinder are transmitted to the apex of a strong triangular spring of tempered steel, F, by a loose steel link. The spring is clamped at its base, G, and its apex carries a thin strip of steel, K, with a scribing style, the movement of which is traced on a smoked-paper chart on a revolving drum mounted at L. At intervals of 20 cm. along the cylinder are plug fittings, one of which is shown at M (Fig. 1*a*), and another in cross-section at N, which are normally used for the insertion of circular windows of quartz, 6·3 mm. in diameter, through which the flame of an explosion as it passes can be photographed. For such photographs a camera with a quartz lens is used, with a revolving drum on which "Lumière" sensitised paper is wrapped. The plug fittings also serve on occasion for the introduction of screen-wires, whereby the passage of flame can be recorded electrically, or for firing-plugs, when it is desired to ignite the mixture otherwise than at the end of the cylinder. Valves at O and P allow of the evacuation of the cylinder and the admission of the explosive mixture.

In carrying out an experiment, the cylinder was filled with the required mixture, prepared beforehand in a gas-holder over glycerol and water. Ignition was effected by a single secondary discharge from an 8-inch induction coil, produced by breaking a current of 5 amps. in the primary circuit. The moment of ignition was recorded on both the pressure chart and the photographic paper, the speeds of revolution of both drums being obtained by means of a tuning fork of 50 frequency.

Results of Experiments.

A. Ignition at One End of the Cylinder.—When ignition was at one end of the cylinder, the time taken for the flame to travel throughout its length, in all the mixtures of methane and air studied, corresponded with the time of attainment of maximum pressure recorded by a manometer at the far end. The time at which the flame reached the far end of the cylinder was recorded either (*a*) by the fusion of a fine screen-wire of copper or (*b*) photographically (at a window 1·0 cm. from the end). The results are given in Table I.

The speed of flame. The mean speed of propagation of flame over the 200-cm. length of the cylinder was for all mixtures considerably faster than the mean speed from the centre to the wall of

TABLE I.

Explosions of Methane–Air Mixtures in a Cylinder.

(Ignition at one end.)

Methane, %.	Time of maximum pressure (sec.).	Time of travel of flame (sec.). By method (*a*).	By method (*b*).
7·15	1·57	—	1·58
8·30	0·76	—	0·76
8·40	0·67	0·67	—
8·75	0·66	0·66	—
9·30	—	0·58	0·55
9·50	0·55	0·55	—
9·75	0·55	0·55	—
9·80	0·56	—	0·56
9·90	0·57	0·57	—
9·95	0·49	—	0·49
10·00	*0·52*	*0·53*	—
10·25	0·60	0·60	0·60
10·90	0·63	0·62	—
11·30	0·89	—	0·89
13·45	2·50	2·53	—

a sphere of 15·6 cm. radius (Wheeler, J., 1918, **113**, 840); thus, fo 9·8% mixture the mean speed was 410 cm. per sec. as compared w 144 cm. per sec. for the sphere. In a sphere, with central igniti the flame moves at a nearly uniform speed until it approaches walls. In a long cylinder, on the other hand, the progress of flame is by no means uniform, and measurements of the mean sp over the whole distance have little significance. This is illustra by the photographic analysis of the movement of flame in a 9·7 methane–air mixture reproduced at (1) on Plate I (much reduced size).

From the times at which the flame first appeared at each wind the mean speed over each successive length of 20 cm. can be c culated. Calculations for mixtures containing 9·6 and 10% methane are recorded in Table II.

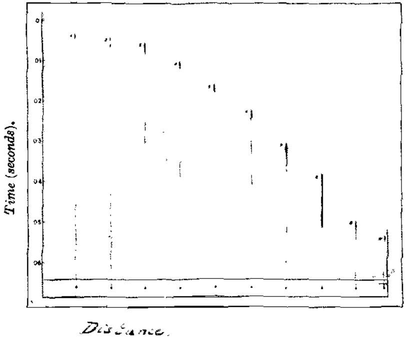
TABLE II.

Speed of Flame in a Long Cylinder.

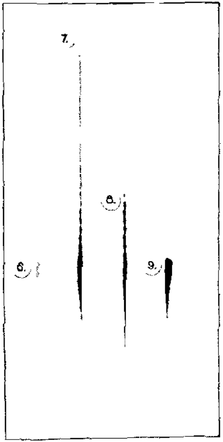
Distance (cm.).	Speed (cm. per sec.). 9·6% CH_4.	10·0% CH_4.	Distance (cm.).	Speed (cm. per sec. 9·6% CH_4.	10·0% C
0— 20	*800*	*1000*	*100—120*	*300*	*333*
20— 40	2000	2000	120—140	210	281
40— 60	1165	1000	140—160	196	181
60— 80	715	500	160—180	181	162
80—100	*345*	*317*	180—*200*	*500*	*385*

These results, which are typical of the most explosive mixture methane and air, show that at the outset the flame darts forwar a rapidly increasing speed. A retardation then occurs, and beco

PLATE I.



(1)
Explosion of a 9·7% methane–air mixture.
Flame at windows along 200-cm. cylinder.



(2)
Similar explosion to (1), showing details
of flame at windows 6 to 9.

[To face p. 3206.]

most marked by the time the flame has travelled about one-third of the length of the cylinder. A comparatively slow speed is then maintained until within 20 cm. of the end of the cylinder, whereupon the flame moves forward more rapidly. The majority of the photographs show that the flame assumes a vibratory character at the end of its travel. In some photographs, vibrations also appear after the flame has travelled half-way along the cylinder. For mixtures containing from 9·5—10·0% of methane, the frequency of the later vibrations, which are always strongly marked (see 2, Plate I), is about 200. When vibrations occur midway along the cylinder, their frequency is about 115.

The development of pressure. In a spherical vessel with central ignition, the flame in mixtures of methane and air containing between 7 and 11% of methane reaches the wall simultaneously at all points, so that the whole of the mixture is inflamed before any appreciable cooling can take place. In a long cylinder, on the other hand, with ignition at one end, part of the flame touches the walls long before propagation is complete, and cooling of products of combustion begins at an early stage. The rate of development of pressure can therefore be expected to be slower than in a sphere, and the maximum pressure to be lower. In Table III the maximum pressures (above atmospheric) recorded for a number of mixtures of methane and air (*a*) in a 16-litre sphere (with central ignition) and (*b*) in the cylinder (capacity about 16 litres) are compared.

TABLE III.

Maximum Pressure on Explosion of Mixtures of Methane and Air in (a) *a Sphere and* (b) *a Cylinder.*

	Maximum pressure, atms.			Maximum pressure, atms.	
CH_4, %.	(*a*).	(*b*).	CH_4, %.	(*a*).	(*b*).
6·05	2·86	1·70	10·30	—	3·87
6·85	4·35	2·04	10·80	6·80	3·54
7·80	5·85	2·72	11·90	6·40	2·72
8·80	6·66	3·74	12·80	5·78	2·24
9·80	6·94	4·00			

The time-pressure records were of two types, dependent on the composition of the mixture. If the mixture contained less than 8 or more than 11% of methane, smooth curves of the type reproduced at A, Fig. 2 were obtained. With 8—11% of methane, the curves showed marked vibrations at their crests (see B, Fig. 2). These vibrations had the same frequency, about 200, as those of the flame as it reached the end of the cylinder. Indeed, the development of pressure throughout corresponded closely with the movement of the flame, as the time-pressure and time-distance curves

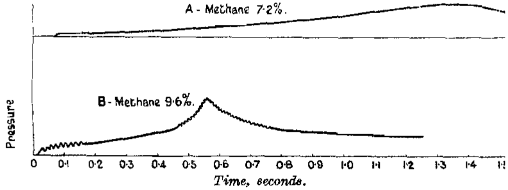
reproduced in Fig. 3 illustrate. Both curves relate to a 10% methane-air mixture, the former showing the development o *pressure up to the time of its maximum, and the latter the time* o passage of the flame from end to end of the cylinder.

Correlation of Flame-movement with Pressure-development.

When comparing the time–pressure and the time–distance curv in Fig. 3, it must be remembered that the latter was obtained fron records of the passage of flame at small windows 20 cm. apart Between any two windows, fluctuations in the movement of th flame may have occurred of which no record was obtained. Never theless, the two curves correspond closely in character and exhibi the following features.

FIG. 2.

Typical time–pressure curves.



(*a*) A rapid rise in pressure, shortly after ignition, correspondin with a rapid movement of flame over the first 20 or 30 cm. Durin this stage, there is but little cooling of the products of combustion since the flame moves rapidly along the axis of the cylinder and bu a small part of its surface comes in contact with the walls (see Par III, following paper).

(*b*) *An arrest in pressure-development, corresponding wit* an arrest in flame-movement. At this point the "skirt" of th flame (see Part III) comes in contact with the walls of the cylinder Following this arrest, both the movement of the flame and th development of pressure are comparatively slow over a distance o about 150 cm.

(*c*) A rapid rise in pressure to a maximum as the flame move rapidly towards the end of the cylinder. Rapid vibrations (omitte from Fig. 3) are shown by both the pressure curves and the flam photographs.

(*d*) At any moment before the flame has travelled throughou the mixture, the fraction of the total distance travelled is greate

flame surface, so long as it is not vibratory, must be advanced along the axis of the cylinder, tailing off towards the walls.

B. Position of Point of Ignition varied.—A series of experiments was made, with mixtures containing between 9·5 and 9·8% of methane, in which the position of the point of ignition was varied. To effect this, the ignition plug was removed from the end of the cylinder and screwed into one or other of the window holes disposed along its length, the electrode points, 4 mm. apart, being carried to the horizontal axis of the cylinder.

Measurements were made of the times taken for the flames to reach each end of the cylinder, of the maximum pressure recorded by a gauge fixed at the end nearer the point of ignition, and of the

Fig. 3.

Comparison of time–pressure and time–distance curves.

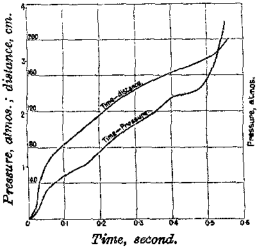
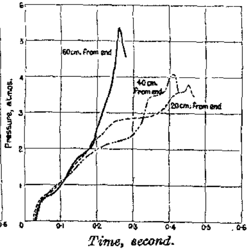


Fig. 4.

Point of ignition varied.



time of attainment of this maximum pressure (" time of explosion "). The results are summarised in Table IV, in which the end of the cylinder to which the pressure gauge was attached is termed A, and the other end B.

In each experiment the maximum pressure was recorded at the moment when flame had reached the end of the longer limb of the cylinder. Unless there was considerable disparity in length between the two limbs, there was a marked tendency for the flames travelling to right and left from the point of ignition to reach the ends of the cylinder simultaneously, and the attainment of maximum pressure could then be said, in general, to synchronise with the complete inflammation of the mixture.

When ignition was effected at a distance of about 40 cm. or less from one end of the cylinder, the flame reached the near end, and was extinguished with consequent rapid cooling of the products of com-

TABLE IV.

Explosions of Methane–Air Mixtures in a Cylinder.

(Position of point of ignition varied.)

Point of ignition.	CH_4, %.	Time (sec.) for flame to travel from point of ignition to End A.	End B.	Max. press. (atm.; above atmospheric).	"Time of explosion" (sec.).
At end A.	9·50	—	—	4·07	0·52
	9·75	—	—	4·35	0·48
	9·90	—	—	4·28	0·50
20 Cm. from A.	9·55	—	0·41	4·07	0·41
	9·40	0·18	0·41	—	—
40 Cm. from A.	9·40	0·25	0·38	—	—
	9·60	—	0·44	3·81	0·44
60 Cm. from A.	9·30	0·27	0·34	—	—
	9·40	0·30	0·35	—	—
	9·60	—	0·27	5·44	0·26
80 Cm. from A.	9·50	0·21	0·21	—	—
	9·85	—	—	5·88	0·19
100 Cm. from A (*i.e.*, midway).	9·50	—	—	5·85—6·12*	0·18
	9·50	0·18	0·19	—	—
	9·55	—	0·24	5·72—5·98*	0·24

* Measurements uncertain owing to vibrations.

bustion, some time before it reached the far end. For this reason the maximum pressure attained was less than when ignition was at the middle. For the same reason, the maximum pressure increased in magnitude as the point of ignition was moved towards the middle of the cylinder, whilst the interval between ignition and the attainment of maximum pressure decreased. The maximum pressure recorded when ignition was at the middle of the cylinder was higher than when ignition was at one end. The three curves reproduced in Fig. 4 represent the rate of rise of pressure when ignition was at a point 20, 40, or 60 cm. from one end of the cylinder.

C. Simultaneous Ignition at Two Points.—A series of experiments was made in which methane–air mixtures containing between 9 and 10% of methane were ignited at some point along the cylinder and at one end simultaneously, a pressure gauge being fixed at the opposite end. The object was to determine whether a higher pressure would be attained than that recorded when ignition was solely at the middle of the cylinder. The results are summarised in Table V.

Typical time–pressure curves are reproduced in Fig. 5, and from curves A, B, and C it will be seen that the rate of rise of pressure to the maximum became more rapid as the second ignition point was moved nearer to the middle of the cylinder (100 cm. from end A). The initial rate of development was then more rapid than with single ignition in any position. When the second ignition point

Table V.

Explosions of Methane–Air Mixtures in a Cylinder.

(Simultaneous ignition at one end and at some point along the cylinder.

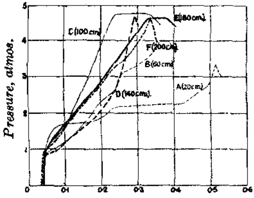
CH_4, %.	Position of second ignition plug (cm. from end plug).	Max. pressure (atms.; above atmospheric).	"Time of explosion" (sec.).
9·75	(Ignition at one end only)	4·35	0·48
9·80	20	3·33	0·52
9·80	60	3·98	0·37—0·39*
9·80	100	4·80	0·24—0·33*
9·80	140	4·70	0·29
9·45	180	4·66	0·33—0·36*
9·75	200	4·66	0·34

* Period of sustained pressure.

was 20 cm. from end A (curve A), there was a long period during which the rate of development of pressure was very slow, and the pressure ultimately attained was considerably lower than when ignition was solely at one end of the cylinder. The maximum pressure with double ignition was obtained when ignition was at one end and at the middle of the cylinder, but this pressure was lower than when ignition was at the middle of the cylinder only.

Fig. 5.

Dual ignition (distances are those of second ignition plug from end plug).



The important factor with respect to the production of pressure on explosion of a given mixture in a long cylinder is the *time taken for the flame to travel throughout the mixture.* When the mixture is ignited simultaneously at two points, the movement of one flame affects the movement of the other, hindering its development (see Part III). *It thus results that the inflammation takes longer to complete when two flames are started simultaneously within the cylinder than when flame spreads from one point along the cylinder only.* The three *time–pressure curves* (B, C, and E in Fig. 5) for explosions started simultaneously at one end of the cylinder and at 60, 100, or 180 cm. from that end, illustrate the retardation of the flames moving towards each other, for the period of maximum pressure is prolonged to a remarkable extent (0·02 to 0·09 sec.) corresponding with the slow approach of the flames.

Part II. The Effect of the Length of the Cylinder.

With a 200-cm. cylinder (10 cm. in diameter), it has been shown that in all explosions of methane–air mixtures containing 8—11% of methane, ignition being at one end of the cylinder, the flames became strongly vibratory towards the end of their travel. In earlier experiments with a cylinder of the same diameter but only 50 cm. long, *no such vibrations* were observed during the explosion of any mixture of methane and air. This accords with observations by Morgan to which reference was made in Part I. An explosion of coal-gas and air in a steel tube 4·45 cm. in diameter and 61 cm. long (ignition being at one end) was strongly vibratory, whereas an explosion of the same mixture in a similar tube of half the length showed no vibrations. Morgan considered the vibrations to be due to two interdependent factors—the rate of heat generation at the flame front and the vibration frequency of the gas space in the explosion vessel.

In order to study this matter more closely, by determining the limit at which an explosion becomes vibratory, arrangements were made for altering the length of our cylinder at will, by means of a piston that could slide within the cylinder and be locked in any position, the piston-head forming a pressure-tight end-plate. The ignition plug was at the centre of the piston-head, and the pressure gauge at the other end of the cylinder. On exploding mixtures of methane and air containing about 9·5% of methane, records were obtained of the maximum pressure developed (P, in atms.), the time of attainment of maximum pressure (T_m), and the time (T_f) taken for the flame to travel throughout the cylinder, the length (l) of which was varied between 2·5 and 200 cm. Some of the results are recorded in Table VI.

TABLE VI.

Explosions of a 9·5% Methane–Air Mixture in Cylinders of Different Lengths (10 *cm. diam.*).

l, cm.	P.	T_m, sec.	T_f, sec.	l, cm.	P.	T_m, sec.	T_f, sec.
2·5	5·8	0·035	0·009	70	4·9	0·27	0·22
3·5	6·1	0·037	0·015	80	4·7	0·31	0·20
5	5·9	0·047	—	100	4·6	0·34	0·30
6	6·3	0·043	0·024	120	4·3	0·38	—
10	6·3	0·07	0·04	140	4·1	0·45	0·44
20	5·9	0·11	0·08	160	3·8	0·48	0·47
30	5·8	0·15	—	165	3·7	0·50	0·49
40	5·5	0·18	—	170	3·7	0·48	0·48
50	5·5	0·20	—	180	4·0	0·49	—
60	5·3	0·24	0·20	200	4·0	0·55	0·55

The critical length of cylinder for the production of a vibratory explosion with a 9·5% methane–air mixture was 140 cm. With shorter lengths, the movement of flame and the rate of production

of pressure were regular, the time–pressure records being characterised by a steady period of maximum pressure lasting from 0·005 sec. for a cylinder 3·5 cm. long to 0·03 sec. when the length was 120 cm. All such explosions were quite silent. When the cylinder was 140 cm. long, or longer, rapid vibrations were usually developed by the flames towards the end of their travel, and, synchronising with these vibrations, the time–pressure records (*e.g.*, B, Fig. 2) showed fluctuations at their crests. All such explosions were accompanied by a shrill screech.

When the explosion was vibratory, the time of attainment of maximum pressure ("time of explosion"), which always corresponded closely with the time taken for the flame front to travel throughout the cylinder, varied as between one experiment and another, performed under what were intended to be identical conditions, within fairly wide limits. For example, when the cylinder was 160 cm. long, the time of explosion was 0·466, 0·596, 0·565, and 0·483 sec. in successive experiments. It would seem that the moment at which vibrations were induced (and the subsequent course of the explosion thereby determined) was affected by slight inadvertent changes in the experimental conditions such, *e.g.*, as the condition of the inner walls of the explosion vessel. Similarly, a slight intentional change in the experimental conditions would transform a silent explosion into a noisy and vibratory one. A 6·85% methane–air mixture, initially at atmospheric pressure, exploded in the 200-cm. cylinder (ignition being at one end), was always silent and non-vibratory (time of explosion, 1·56 sec.), but when the initial pressure was increased to 3·6 atm. (absolute) the explosion was vibratory (time of explosion, 1·95 sec.). Similar results for pentane–air mixtures have been recorded by Maxwell and Wheeler (*J. Inst. Pet. Tech.*, 1928, **14**, 175).

The vibrations that occur, following the "uniform movement," when an explosive mixture is ignited at the open end of a long tube closed at the other end, have been shown by Mason and Wheeler (J., 1920, **117**, 36) to be due to resonance in the column of gases ahead of the flame, their frequency corresponding with that of the fundamental tone of the tube. The same explanation can apply to these closed-tube vibratory explosions, although on what the establishment of resonance depends is not clear. Morgan's (*loc. cit.*) suggestion, which appears to be accepted by Egerton and Gates (*Proc. Roy. Soc.*, 1927, *A*, **116**, 524), that the rate of heat generation at the flame front is the main factor involved, receives support from the fact that in a cylinder 120 cm. long the explosion of a 5·75% ethane–air mixture (time of explosion, 0·215 sec.) is vibratory, whereas that of a 9·5% methane–air mixture (time of explosion,

0·386 sec.) is not. On the other hand, some of Maxwell and Wheeler's (*loc. cit.*) results are at variance with this suggestion, for they found that, under the same conditions of experiment, the explosion of a 3·5% pentane–air mixture (time of explosion, 0·19 sec.) was vibratory, whereas that of a 2·95% benzene–air mixture (time of explosion, 0·17 sec.) was not. It would seem reasonable to believe that with a given explosive mixture, say a 9·5% methane–air mixture, the establishment of resonance in the column of gases ahead of the flame would depend, *ceteris paribus*, upon the rapidity with which the column was compressed. Thus it would depend upon the speed acquired by the flame front, which in turn would depend on the length of the cylinder. When explosions of different gases under the same conditions are compared, however, this explanation is insufficient. We believe the character of the reactions taking place behind the flame front to have an important bearing on the matter; we are now investigating this subject.

The relationship between the time of explosion and the length of the cylinder (for 9·5% methane–air mixtures) is shown in Table VI. There was close correspondence between the time of explosion and the time of passage of flame when the explosions were vibratory, *i.e.*, when the cylinder was 140 cm. long or longer. In the shorter cylinders, the flame front, travelling without vibrations, apparently reached the end before the attainment of maximum pressure. This is explicable by reason of the shape of the flame front which, when travelling in a horizontal tube, is inclined, the upper portion being in advance. After the flame has appeared at a window at the end of the horizontal axis, it still has to travel into the lower portion of the tube.

The time of explosion does not increase proportionally with the length of the cylinder, as it would if the mean speed of the flame were constant, but is less by so much as the mean speed of the flame is greater in the longer cylinders. This greater speed is due to the greater freedom of movement, at the outset of the explosion, of the unburnt gas ahead of the flame in the longer cylinders (see Part III), the conditions during the early stages of the spread of flame approximating more and more to those of constant pressure as the length of the cylinder is increased.

We wish to thank Mr. W. A. Batley, M.Sc., of the Department of Fuel Technology of Sheffield University, for considerable help with the experiments described in this paper. This work has been carried out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish the results.

Safety in Mines Research Laboratories,
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CCCCXXVI.—*Explosions in Closed Cylinders. Part III. The Manner of Movement of Flame.*

By Oliver Coligny de Champfleur Ellis and Richard Vernon Wheeler.

Some of the phenomena of explosions of methane and air in closed cylinders described in Parts I and II (preceding paper) can be explained by a study of the movements of flames under similar conditions by means of "snapshot" photographs on a stationary plate (see J., 1925, **127**, 760). In the examples reproduced in this paper, the flames are of carbon monoxide with oxygen, because their high actinic value renders them so serviceable for photographic analysis. The manner of movement of flame in mixtures of methane and air is essentially the same.

Ignition at One End of the Cylinder (compare Part I, A).—The photographs reproduced on Plate I are successive snapshots, at equal intervals of 4·1 millisecs. after ignition, of flame travelling in a mixture $10CO + O_2$, saturated with water vapour at 13·5°, after ignition at the centre of one end of a glass cylinder, 2·5 cm. in diameter and 20·3 cm. long, closed at both ends by rubber pads. The speed of flame in this mixture is comparable with that in a 9·5% methane–air mixture.

In the first snapshot, the flame appears as a small hemisphere centred on the point of ignition. In Fig. 2, no part of the tubular flame surface has as yet made contact with the walls of the cylinder, but its domed front has made rapid progress along the axis. In Fig. 3, the domed front has travelled still further, but the fringe of the luminous "skirt" has been extinguished. In Fig. 4, and thereafter, only the front portion of the flame surface remains, and that has changed its shape, having been turned inside-out owing to the sudden cooling of products of combustion behind it when the whole of the "skirt" came in contact with the walls of the cylinder.

The rapidly increasing speed of flame and development of pressure during the early stages of the explosion, remarked upon in Part I, are thus seen to be due to the increasing area of flame surface; the marked retardation and subsequent comparatively slow movement of flame and development of pressure are due to the sudden decrease in the area of the flame surface, consequent on the contact of all but its front with the walls of the cylinder, and to the sudden increase in the area over which the products of combustion are cooling. Although discussion of the matter is outside the scope of the present paper, we should mention that we regard the initial retardation of movement of the flame surface as being due to the retardation of

movement of the medium in which it is travelling. This initial retardation is accentuated by the sudden cooling of the products of combustion behind the flame surface (see *Fuel*, 1928, 7, 195; compare Payman, *Proc. Roy. Soc.*, 1928, *A*, **120**, 90).

The individual snapshots of Plate I, together with subsequent snapshots at equal intervals until the flame had wholly expired, are shown as a composite photograph on Plate II. A record of the same flame taken on a revolving film is reproduced for comparison. The sudden retardation in the progress of the flame occurred when it had travelled about one-third of the length of the cylinder. Thereafter, its speed was nearly uniform until it reached the end. In this respect the explosion of $10CO + O_2$ in this comparatively short cylinder differed from the 9·5% methane–air explosions in a cylinder 10 cm. in diameter and 200 cm. long (described in Part I), inasmuch as in the latter the flames exhibited vibrations, and an increased speed, towards the end of their travel. In a glass cylinder 2 cm. in diameter and 40 cm. long, the flames in the mixture $10CO + O_2$ sometimes vibrated.

Position of Point of Ignition varied (compare Part I, B).—The effect of varying the point of ignition is illustrated in Figs. 1, 2, and 3 on Plate III. For these experiments the cylinder was 2 cm. in diameter and 40 cm. long, and the explosive mixture used was $10CO + O_2$. Ignition, on the axis of the cylinder, was at one end (Fig. 1), at the middle (Fig. 2), and midway between the middle and one end (Fig. 3). With ignition at the middle, the flame surfaces vibrated, and their mean speed increased, towards the end of their travel. The flame surface, being a mobile source of pressure in an enclosed space, tends to centre itself within the cylinder, so that when ignition is not at the middle it moves most rapidly towards the region of greatest volume. Cooling does not occur until the flame surface touches the walls, but, owing to its elongated shape at that moment (see Fig. 3, Plate III), cooling is then considerable. For this reason, and because of the sudden diminution in area of the flame surface, there is a sudden retardation in the movement of the flame (and in the development of pressure). The flame continues to propagate on two fronts (so that the rate of production of pressure tends to be double what it is when ignition is at one end of the cylinder), travelling faster towards the farther than towards the nearer end. It expires first at the nearer end, the system at that moment suffering both a reduced production of energy and an increased dissipation due to cooling. The speed of the remaining flame surface is therefore retarded. It thus results that, although when ignition is asymmetric the two flame surfaces near· reach the two ends of the cylinder simultaneously, there is a comparatively

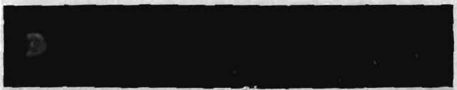

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

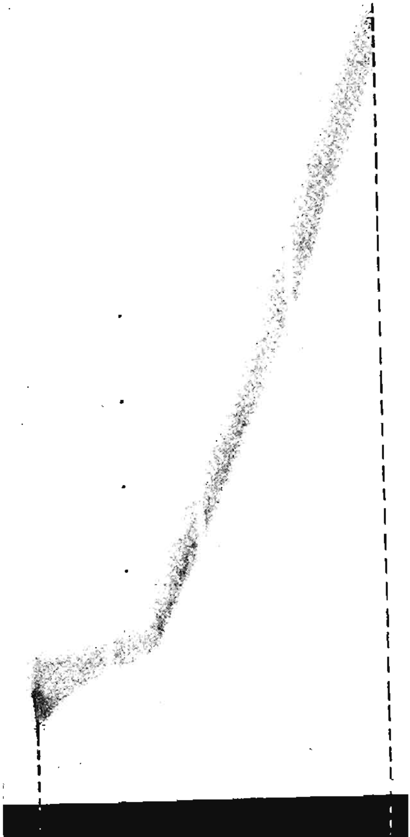

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Plate III.

Fig. 1.

Fig. 2.

Fig. 3.

long interval between the expiration of the flame at the nearer end and its final expiration at the farther end. The more asymmetric the point of ignition, the greater is this interval, and the less, in consequence, is the maximum pressure developed.

Simultaneous Ignition at Two Points (compare Part I, C).—When an explosive mixture within a cylinder is ignited simultaneously at two points, not too close together, the initial rate of rise of pressure should be twice as fast as with single ignition unless the two flames hinder each other's development. Actually, the two flames do hinder each other, each developing a smaller surface area in a given time than it would if the other were absent. This is illustrated in Fig. 4, Plate III, which is a composite photograph of three successive snapshots, at equal intervals of 9·63 millisecs. after ignition, of flames in a mixture $13CO + O_2$, saturated with water vapour at 14°, contained in a closed horizontal glass tube 4 cm. in diameter and 32 cm. long. The mixture was ignited simultaneously at the middle of the cylinder and midway between the middle and one end. The two continuous flame surfaces tend to dispose themselves symmetrically. That on the left centres itself within the left-hand half of the tube, not within the tube as a whole as it would tend to do if it were alone. The right-hand flame surface moves bodily towards the right.

When contact occurs between the flame surfaces and the walls of the cylinder, the area of contact is nearly twice that when ignition is at one point only, and the rate of cooling is nearly twice as great. The net rise of pressure subsequently is therefore small, though the pressure is maintained from four sources whereas with single ignition there are but two. Figs. 5, 6, and 7 on Plate III are single snapshots (taken, respectively, 48·15, 57·78, and 62·59 millisecs. after ignition) of the flame surfaces after contact with the walls of the cylinder had occurred. They show the remarkably slow approach of the two inner flame surfaces towards each other.

With a 25% carbon monoxide–air mixture, saturated with water vapour at 11·8°, a number of experiments were made with different conditions of ignition in a glass cylinder 6 cm. in diameter and 32 cm. long. The durations of the flames under these different conditions are recorded in Table I.

The shortest duration of flame was thus with symmetrical double ignition at such a distance from the ends of the cylinder that there is no initial cooling; and the longest was with single-end ignition.

The Effect of the Length of the Cylinder (compare Part II).—Fig. 1 on Plate IV shows a succession of snapshots, at intervals of 4·1 millisecs. after ignition, of the flame in a mixture $10CO + O_2$, saturated with moisture at 15°, ignited at the end of a vertical closed

TABLE I.

Carbon Monoxide and Air (25% CO), *ignited within a Horizontal Glass Cylinder* (6 × 32 cm.).

	Distance along tube, cm. 0.	8.	16.	24.	32.	Duration of flam centisecs.
Ignition at points indicated (I).	I	—	—	—	—	22·1
	I	I	—	—	—	17·5
	I	—	I	—	—	12·3
	I	—	—	I	—	11·0
	I	—	—	—	I	14·2
	—	I	—	—	—	15·1
	—	I	I	—	—	11·4
	—	I	—	I	—	9·3
	—	—	I	—	—	14·4

cylinder, 5·0 cm. in diameter and 17 cm. long. The cylinder w placed vertically to secure symmetry of the flame surfaces and th render their movement during the later stages clearer than it when the cylinder is horizontal (see, *e.g.*, Fig. 1, Plate III). Fig. Plate IV, should be compared with Figs. 2 and 3, for which t conditions of experiment were identical save that the cylinder w reduced in length to 12 cm. (Fig. 2) and 9·5 cm. (Fig. 3). It is evide that the greater the length of the cylinder the more freely does t flame surface move along its axis. It is evident, also, that at t moment when the flame surface has made contact with the wal and rapid cooling of the products of combustion has begun, greater proportion of the mixture has been burnt in the shorte than in the longest cylinder, so that a higher maximum pressu would be recorded in the former.

The experiments described in this paper were carried out in co nexion with work that we are doing for the Safety in Mines Resear Board, to whom our thanks are due for permission to publish the results.

SAFETY IN MINES RESEARCH LABORATORIES,
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CCCCXXVII.—*Acid and Salt Effects in Catalysed Reactions. Part XVIII. The Dynamics of Autocatalysed Ester Hydrolysis.*

By HARRY MEDFORTH DAWSON and WILLIAM LOWSON.

RECENT experiments by the authors (this vol., p. 2146) have show that the initial speed of the hydrolysis of ethyl acetate with hydr chloric acid as catalyst is proportional to the concentration of t acid when this is varied between 0·0002 and 0·2 mol. per litre.

the *concentration of the hydrochloric acid is less than* 0·01 mol. per litre, the course of the reaction is modified by the catalytic action due to the acetic acid produced. The relative importance of this autocatalytic effect increases as the concentration of the hydrochloric acid diminishes, and it is not possible in practice to determine the initial velocity of the reaction when this concentration falls below 0·0002 mol. per litre.

The present experiments are, for the most part, concerned with the course of the reaction when foreign catalysts are absent, *i.e.*, when the only catalytic effects involved are those which are attributable, directly or indirectly, to the solvent or to the acetic acid which is set free in the reaction. In this connexion, reference should be made to the experiments of Wijs (*Z. physikal. Chem.*, 1893, **11**, 492; **12**, 514) on the autohydrolysis of methyl acetate, in which the progress of the reaction was followed by measurements of the electrical conductivity of the solution, and it was shown that the reaction velocity passed through a minimum value. The observations were, however, confined to a very small period in the early stages of the reaction, but this was sufficient for the main object of the experiments, which was to obtain a value for the ionisation constant of water.

In its entirety, the autocatalytic hydrolysis of an ester such as ethyl acetate represents a complex process in which the reaction velocity passes through a minimum and a maximum value. The attainment of maximum velocity is not in any way connected with the reversibility of the reaction, although this alone would of course suffice to determine the incidence of a maximum. If, however, the reverse reaction has to be taken into account, the mathematical treatment of the problem becomes extremely complex, and for this reason the investigation has been confined to that phase of the complete reaction for which the influence of the oppositely directed esterification process can be neglected. Within these limits, and in accordance with current views relating to catalytic effects, the general equation for the reaction velocity may be written

$$dx/dt = \{k_h[H^+] + k_{OH}[OH^-] + k_w[H_2O] + k_a[Ac^-] + k_m[HAc]\}\,(a - x)[H_2O] \quad . \quad . \quad (1)$$

in which the catalytic coefficients are represented by the usual symbols and $(a - x)$ is the concentration of the ester after time t. Since the concentrations of the several catalytic entities are connected by $[H^+].[OH^-] = K_w$, $[Ac^-] = [H^+] - [OH^-]$, and $[HAc] = x - [Ac^-]$, equation (1) may be written

$$dx/dt = \{(k_h - k_m + k_a)[H^+] + (k_{OH} + k_m - k_a)K_w/[H^+] + k_m x + k_w[H_2O]\}\,(a - x)[H_2O]$$

and from a consideration of the relative values of $k'_h = 6{\cdot}5 \times 10^{-3}$ $k'_{OH} = 6{\cdot}5$, $k'_m = 1{\cdot}5 \times 10^{-6}$, $k'_a = 2 \times 10^{-7}$, and k'_w, which is too small to have a measurable value assigned to it, it may be readily shown that the equation may be further reduced to the form

$$dx/dt = \{k'_h[\mathrm{H}^+] + k'_{OH}K_w/[\mathrm{H}^+]\}\,(a - x) \quad . \quad . \quad (2)$$

where $k'_h = k_h[\mathrm{H_2O}]$ and $k'_{OH} = k_{OH}[\mathrm{H_2O}]$.

In terms of this equation it is convenient to distinguish two successive stages of the autocatalysed reaction. In the first stage the catalytic effect corresponds with the joint action of the hydrogen and the hydroxyl ion, and the concentration of the ester is practically constant. In the second stage the catalytic action is confined to the hydrogen ion, and the concentration of the ester gradually diminishes. There is, of course, no breach of continuity in passing from the first to the second stage, but it is convenient, although more or less arbitrary, to select as the end of the first stage that point at which the catalytic effect of the hydroxyl ion has fallen to 1% of the catalytic effect due to the hydrogen ion.

Before proceeding to the further examination of equation (2) reference may be made to the nature of the experimental observations. The solution of the ester (40 c.c. per litre = $0{\cdot}412M$) was prepared by dissolving carefully purified ethyl acetate in conductivity water, the temperature being kept at 25·0°. The acetic acid formed was determined after suitable time intervals by titration. In the early stages of the reaction, 25 c.c. samples were titrated with $0{\cdot}01N$-alkali, and in the later stages, 10 c.c. samples with $0{\cdot}1N$-alkali.

The earlier experiments showed wide differences in the results obtained; for instance, the time required for the production of acetic acid in $0{\cdot}0002M$ concentration varied from about 3000 to 10,000 minutes. Investigation of the cause of these discrepancies showed that the slower speeds of the reaction were mainly, if not entirely, due to the retarding effect of alkali from the walls of the glass containing vessel. The later experiments were therefore carried out in fused silica vessels, and it was thus possible to obtain reproducible results without difficulty. In order to acquire information relative to the influence of small quantities of alkali, parallel experiments in silica flasks were made with ester solutions to which various small quantities of sodium hydroxide were added. It may be readily shown that the hydroxide is rapidly converted into acetate, and that the course of the reaction as represented by the x–t curve is sensibly the same as if the equivalent amount of sodium acetate had been added at the outset.

In the actual application of equation (2), it has been found convenient express the hydrogen-ion concentration of the acid solution in rms of the ionisation constant of the acid. If $[H^+] = rK$, then $[A] = r^2K$, and the total concentration of the acid is $r(r + 1)K$. ıis quantity r may be termed the ionisation ratio, the relation of ıich to the degree of ionisation is given by $r = (1 - \alpha)/\alpha$ or $= 1/(r + 1)$. In terms of r, the expression for the ionisation nstant takes the form $K = c/r(r + 1)$, where c is the total acid ncentration.

First Stage of the Autocatalysed Reaction.—The quantity of acetic id formed at the end of the first stage is far too small to be deterıned titrimetrically and our concern with this stage is therefore nited to the estimation of the period of time which it occupies. ıe equation for the reaction velocity is

$$dx/dt = \{k'_h[H^+] + k'_{OH}K_w/[H^+]\}\ a \quad . \quad . \quad . \quad (3)$$

d when the acid produced by the reaction is fully ionised, or $[H^+] = x$, this can be integrated quite simply (compare Dawson, , 1927, 458). This, however, is no longer the case when the acid rmed is weak and its hydrogen-ion concentration is given by $[H^+] = \sqrt{(K/2)^2 + Kx} - K/2$; in these circumstances the produre followed in the calculation of the required time involves nsiderations which are associated with the catenary form of the log $[H^+]$ curve. The method employed is general in the sense at it may be applied in the case of all autocatalysed reactions of nilar type.

The hydrogen-ion concentration at which the reaction velocity ısses through its minimum value is given by $[H^+]_i = \sqrt{k'_{OH} . K_w/k'_h}$, and if K_w is taken as 10^{-14}, we obtain $[H^+]_i =$ 32 $\times 10^{-5}$, or since the value of K for acetic acid in $0{\cdot}4M$-ethyl etate solution is $1{\cdot}6 \times 10^{-5}$, $[H^+]_i = 0{\cdot}2K$, or $r_i = 0{\cdot}2$.

If the hydrogen-ion concentration is expressed in terms of $[H^+]_i$ ch that $[H^+]/[H^+]_i = n$, then equation (3) may be written as

$$dx/dt = k'_h[H^+]_i(n + 1/n)a \quad . \quad . \quad . \quad . \quad (4)$$

cording to which 99% of the total catalytic effect is due to the ·drogen ion when $n = 10$, *i.e.*, when $[H^+] = 2K$. The value $= 2$, which corresponds with $x = 6K$, may thus be identified with e end of the first stage of the reaction. For the calculation of e time required to reach this point, the complete stage may be vided into a series of small intervals, Δt, for each of which $\Delta x = \overline{(r + 1)}K = K\Delta q$, where q measures the concentration of the id in terms of K. If, now, $\bar{v}$ is the mean velocity for the interval

characterised by the mean reduced hydrogen-ion concentration $\bar{n}$, then according to equation (4) we have

$$\Delta t = \Delta x/\bar{v} = K\Delta q/[k'_{h}[H^{+}]_{i}(\bar{n} + 1/\bar{n})a]$$

Substituting $a = 0{\cdot}412$, $k'_{h} = 6{\cdot}5 \times 10^{-3}$, and $[H^{+}]_{i} = 0{\cdot}2K$, we have

$$\Delta t = 1870\Delta q/(n + 1/n),$$

whence the time required for the first stage is given by

$$t_1 = 1870\Sigma_{q=0}^{q=6}\Delta q/(n + 1/\bar{n}) \quad . \quad . \quad . \quad . \quad (5)$$

in which $\bar{n} = \bar{r}/r_i$ where $\bar{r}$ is the mean value of r for the interva for which the mean reduced hydrogen-ion concentration is $\bar{n}$. Th smaller the values of Δt and Δq, the greater will be the accurac of t_1 given by equation (5). For the present purpose it is, however sufficient to divide the first stage of the reaction into ten intervals each of which corresponds with $\Delta r = 0{\cdot}2$. In this case the en of the first interval coincides with the point of minimum velocity To illustrate the exact procedure and the nature of the results, th detailed figures are recorded in Table I. The first column give the initial and final values of r for each interval; the second, th value of $\bar{n} = \bar{r}/r_i$; the third, that of $(\bar{n} + 1/\bar{n})$; the fourth, th initial and final values of q; the fifth, the value of Δq; and th sixth, that of Δt (in mins.).

TABLE I.

Autocatalysis : First Stage.

r'—r''.	$\bar{n}$.	$\bar{n} + 1/\bar{n}$.	q'—q''.	Δq.	Δt.
0·0—0·2	0·5	2·50	0·00—0·24	0·24	180
0·2—0·4	1·5	2·17	0·24—0·56	0·32	276
0·4—0·6	2·5	2·90	0·56—0·96	0·40	258
0·6—0·8	3·5	3·79	0·96—1·44	0·48	237
0·8—1·0	4·5	4·72	1·44—2·00	0·56	222
1·0—1·2	5·5	5·68	2·00—2·64	0·64	211
1·2—1·4	6·5	6·65	2·64—3·36	0·72	202
1·4—1·6	7·5	7·63	3·36—4·16	0·80	196
1·6—1·8	8·5	8·62	4·16—5·04	0·88	191
1·8—2·0	9·5	9·61	5·04—6·00	0·96	187

According to the table, the time required for the completion the first stage of the reaction is $\Sigma\Delta t = 2160$ minutes. It m further be noted that the value of Δt for equal successive chan in the hydrogen-ion concentration diminishes regularly from t *M.V.* point onwards, *i.e.*, after the first interval. For the ith interv $\Delta q = 0{\cdot}16 + 0{\cdot}08i$, and since $\bar{n}$ approximates to i as the lat increases, it follows that Δt approaches a limiting value $1870 \times 0{\cdot}08 = 149{\cdot}6$ minutes.

When the solution of the ester contains a small quantity

sodium acetate, the hydrogen-ion concentration corresponding with a given concentration of acetic acid (x) is reduced. If the concentration of the acetate (S mols. per litre) is expressed in terms of K, such that $S = mK$, then from $[HA] = x - [H^+] = [H^+](S + [H^+])/K$, we obtain $x = r(r + 1 + m)K$, or $q = r(r + 1 + m)$. Since the end of the first stage is reached when $r = 2$, it follows that the concentration of the acetic acid in the solution at this point increases with the quantity of sodium acetate present. The relation between the velocity of the autocatalysed reaction and the hydrogen-ion concentration is not, however, affected thereby, and the presence of sodium acetate makes no difference to the method described above for the calculation of the time which is occupied by the first stage of the autocatalysis. The values of q and t_1 for the quantities ($m = S/K$) of sodium acetate actually used in the experiments to be described are as follows:

m =	0	1·2	3·0	6·0
q =	6·0	8·4	12·0	18·0
t_1 =	2160	3215	4800	7450 mins.

Second Stage of the Autocatalysed Reaction.—The beginning of this stage is characterised by the circumstance that the hydroxyl ion ceases to play any sensible part in the hydrolysis. The equation for the reaction velocity may therefore be written

$$dx/dt = k'_h[H^+](a - x) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

As in the case of the first stage, the form of the expression which gives the connexion between x and t is the same whether the hydrolysis takes place in pure water or in a solution which contains a small amount of alkali (sodium acetate). In these circumstances, it seems preferable to consider the general case in which the solution contains S mols. of acetate per litre. Since the hydrogen-ion concentration is given by $[H^+] = \sqrt{(K + S)^2/4 + Kx} - (K + S)/2$, the previous equation may be put in the form

$$dx/dt = k'_h(a - x)(\sqrt{b^2 + Kx} - b) \quad . \quad . \quad (6a)$$

where $b = (K + S)/2$. Replacing $\sqrt{b^2 + Kx}$ by y, equation (6a) may be written

$$k'_h.dt = 2y\,.\,dy/(Ka + b^2 - y^2)(y - b),$$

which, on integration by the method of partial fractions, gives

$$k'_h t = \frac{2b}{Ka}\log(y - b) - \frac{1}{\sqrt{Ka + b^2} - b}\log(\sqrt{Ka + b^2} - y) + \frac{1}{\sqrt{Ka + b^2} + b}\log(\sqrt{Ka + b^2} + y) + \text{const.}$$

Replacing y by its equivalent in terms of x, then for initial and

final values of x and t represented respectively by x', t', and x'' t'', this becomes

$$t'' - t' = \frac{1}{k'_h}\left\{\frac{2b}{Ka}\log\frac{\sqrt{b^2 + Kx''} - b}{\sqrt{b^2 + Kx'} - b} + \frac{1}{\sqrt{b^2 + Ka} - b}\log\frac{\sqrt{b^2 + Ka} - \sqrt{b^2 + Kx'}}{\sqrt{b^2 + Ka} - \sqrt{b^2 + Kx''}} + \frac{1}{\sqrt{b^2 + Ka} + b}\log\frac{\sqrt{b^2 + Ka} + \sqrt{b^2 + Kx''}}{\sqrt{b^2 + Ka} + \sqrt{b^2 + Kx'}}\right\} \quad . \quad . \quad . \quad . \quad (7)$$

In accordance with this equation, t'' may be used to denote the time required for the reaction to proceed from the end of the first stage ($[H^+] = 2K$) to any point in the second stage. For the later phases of the second stage in the absence of sodium acetate, the above equation reduces to the form

$$t'' - t' = \frac{1}{k'_h\sqrt{Ka}}\left\{\log\frac{\sqrt{a} + \sqrt{x''}}{\sqrt{a} + \sqrt{x'}} - \log\frac{\sqrt{a} - \sqrt{x''}}{\sqrt{a} - \sqrt{x'}}\right\} \quad (8)$$

which is identical with the equation previously derived (Dawson and Lowson, J., 1927, 2107) for the hydrolysis of ethyl acetate with acetic acid ($0{\cdot}1N$) as catalyst. Equation (8) follows, in fact directly from eqnation (6) when the concentration of the acetic acid is large enough to permit of the substitution of $\sqrt{Kx}$ for $[H^+]$ In these circumstances,

$$v = k'_h\sqrt{Kx}\,(a - x)$$

whence $$dv/dx = k'_h\sqrt{K}(a/2\sqrt{x} - 3\sqrt{x}/2) \quad . \quad . \quad . \quad (9)$$

according to which the reaction velocity passes through a maximum when $x = a/3$. Under the conditions of our experiments this maximum is reached before the reverse reaction begins to have any appreciable influence on the course of the hydrolysis.

EXPERIMENTAL.

With one exception the glass vessels used in our earlier experiments were found to retard the autocatalytic hydrolysis as compared with the reaction in silica vessels. In the exceptional case the results were practically the same as for the silica flasks. Our experience in this connexion would suggest that the determination of the amount of acid produced by autohydrolysis of an ester in a given time might be made the basis of a practical method for the comparison of the " alkalinities " of samples of glass.

Table II gives the results for the early stages of autohydrolysis in silica flasks with and without the addition of alkali. For each experiment the first column of figures shows the number of c.c. of $0{\cdot}01N$-sodium hydroxide required for the titration of 25 c.c. of the ester solution; the second gives the acetic acid concentrations in

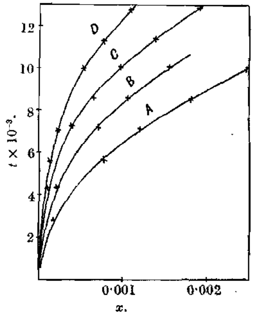
mols. per litre, and the third the corresponding time intervals (minutes $\times 10^{-3}$). The calculated times in the fourth column represent the sum of t_1 and t_2, where t_1 is the time occupied by the first stage and t_2 that required by the second stage; these numbers were derived from the theoretical x–t curves.

TABLE II.

Titre.	$x \cdot 10^3$.	$t \cdot 10^{-3}$ (obs.).	$t \cdot 10^{-3}$ (calc.).	Titre.	$x \cdot 10^3$.	$t \cdot 10^{-3}$ (obs.).	$t \cdot 10^{-3}$ (calc.).
A. NaAc = nil.				*B*. NaAc = $19 \times 10^{-6}N$.			
0·45	0·18	2·80	2·95	0·50	0·20	4·29	3·85
1·95	0·78	5·60	6·05	1·80	0·72	7·16	6·89
3·05	1·22	7·12	7·35	2·70	1·08	8·57	8·10
4·57	1·83	8·48	8·90	3·90	1·56	10·00	9·40
6·25	2·50	10·00	10·40	*C*. NaAc = $48 \times 10^{-6}N$.			
D. NaAc = $96 \times 10^{-6}N$.				0·25	0·10	4·3	3·5
0·32	0·13	5·58	5·0	1·00	0·40	7·20	6·7
0·60	0·24	7·02	6·9	1·65	0·66	8·55	8·1
1·35	0·54	9·99	9·75	2·48	0·99	10·00	9·5
1·95	0·78	11·3	11·2	3·48	1·39	11·4	10·9
2·75	1·10	12·7	12·7	4·80	1·92	12·9	12·6

In comparing the calculated and observed times in the above table it should be recognised that the probable accuracy of the recorded acetic acid concentrations increases as the reaction proceeds, and that the error attaching to the first recorded values may be considerable. It appears that the observed rate of hydrolysis is somewhat more rapid than the theoretical in experiment A, and rather less rapid in B and C, whilst the agreement is very close in experiment D. The fact that the time-differences in A, B, and C are nearly independent of the amount of acetic acid formed suggests that the deviations are associated with the first stage of the autohydrolysis, and it seems probable that they are to be attributed to variations in the purity of the samples of conductivity water used in the several experiments. The experimental x–t curves are shown in Fig. 1.

FIG. 1.



Curves showing the rate of formation of acetic acid by autohydrolysis of ethyl acetate; (A) *in pure water;* (B), (C), *and* (D) *in presence of* 0·000019, 0·000048, *and* 0·000096 *mol. of sodium acetate per litre, respectively.*

Table III gives the results for an extended autocatalytic experiment in which the hydrolysis was allowed to proceed until the influence of the reverse reaction could no longer be ignored. Col. 1 shows the concentration (x) of the acetic acid formed (mols./litre), col. 2 the corresponding observed time interval (minutes $\times 10^{-3}$), and col. 3 the calculated time $t = t_1 + t_2$ derived by the method already explained.

TABLE III.

$x \cdot 10^3$.	$t \cdot 10^{-3}$, obs.	$t \cdot 10^{-3}$, calc.	$x \cdot 10^3$.	$t \cdot 10^{-3}$, obs.	$t \cdot 10^{-3}$, calc.
0·25	10·0	10·4	8·74	61·8	61·5
0·42	12·8	14·0	10·19	67·5	67·2
1·04	20·0	20·6	12·06	75·1	74·5
1·88	27·2	27·5	13·86	81·9	81·5
2·75	33·0	33·0	16·05	90·6	89·8
3·97	40·2	39·5	17·8	97·6	96·5
5·36	47·4	47·2	19·6	105·0	103·5
6·51	53·1	52·5	21·37	112·5	110·5
7·72	60·7	59·8	22·6	117·9	116·0

The above experiment was continued until about 50% of the original ester had been hydrolysed, at which point the velocity of the reverse reaction is about 1/70th of that of the hydrolytic process. This point may thus be taken to represent approximately the end-point of the reaction in so far as the validity of the equation derived for the second stage in the autohydrolysis is concerned. The tabulated numbers show that the observed progress of the reaction is in close agreement with the combined requirements of equations (5) and (7). It may be inferred that the course of the reaction can be interpreted in terms of the catalytic action of the hydrogen and hydroxyl ions, and that the speed of the uncatalysed reaction and the catalytic activity of the water molecules are too small to be measured.

With reference to the variations in velocity during the autohydrolysis, it may be noted that the maximum velocity given by $v_{max.} = k'_h\sqrt{K}x(a - x)$ with $x = a/3$ is $2{\cdot}64 \times 10^{-6}$ mol. per litre per minute, and the minimum velocity given by $v_{min.} = 2a\sqrt{k'_h k'_{OH} K_w}$ is $1{\cdot}69 \times 10^{-8}$ mol. per litre per minute. The ratio of these velocities is thus proportional to the square root of the ester concentration, and for the concentration used in our experiments is equal to 156.

Summary.

The autocatalysed hydrolysis of ethyl acetate, in so far as this is not appreciably affected by the reverse reaction, has been studied by experiments in fused silica vessels.

The reaction may be divided into two stages, in the first of which the velocity is determined by the joint catalytic action of the

hydrogen and hydroxyl ions, and in the second by the catalytic activity of the hydrogen ion.

Equations are derived from which the time required to reach any given point may be calculated.

The retarding influence of small amounts of alkali is shown to be in accord with theoretical requirements.

It would seem that the speed of the uncatalysed reaction and the catalytic activity of the water molecules are too small to have any measurable influence on the course of the reaction.

THE UNIVERSITY, LEEDS. [*Received, October 17th*, 1928.]

CCCCXXVIII.—*Stability of Ferrous Sulphate Solutions and their Use in Standardising Permanganate.*

By JOHN ALBERT NEWTON FRIEND and ERIC GEORGE KEMP PRITCHETT.

FOR many years it has been known that dilute, acidified solutions of ferrous sulphate are very resistant at the ordinary temperature to oxidation by free air or oxygen. The first to study the subject systematically appears to have been McBain (*J. Physical Chem.*, 1901, **5**, 623), who introduced oxygenated water into bottles containing solutions of ferrous sulphate in an inert atmosphere. He observed that the reaction was approximately unimolecular, the rate of oxidation being proportional to the oxygen concentration, and rising rapidly both with the temperature and with concentration of the ferrous sulphate solution. He also found that sulphuric acid ranging in concentration from $N/50$ to N (referred to as $N/2$ in the text, but apparently by a typographical error) exerted a small but definite retarding action.

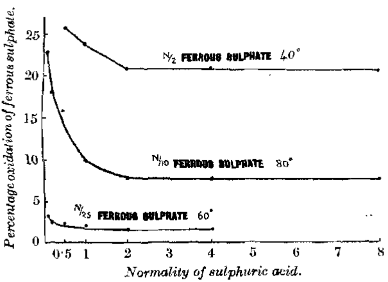
Some of these observations have been confirmed and extended by other investigators (see Peters and Moody, *Amer. J. Sci.*, 1901, **12**, 369; Phelps, *Z. anorg. Chem.*, 1904, **38**, 110; Müller and Kapeller, *Z. Elektrochem.*, 1908, **14**, 76; Baskerville and Stevenson, *J. Amer. Chem. Soc.*, 1911, **33**, 1104), notably by Ennos (*Proc. Camb. Phil. Soc.*, 1913, **17**, 182), who concluded that atmospheric oxidation takes place *via* the un-ionised portion of the ferrous salt, and by Warynski (*Ann. Chim. Analyt.*, 1909, **14**, 45) and Banerjee (*Z. anorg. Chem.*, 1923, **128**, 343), who have studied the retarding or accelerating influence of dissolved salts and free acids, but in very dilute solution only.

On the other hand, Reedy and Machin (*J. Ind. Eng. Chem.*, 1923, **15**, 1271), in contrast to McBain, found that on bubbling air through

solutions of ferrous sulphate ranging in concentration from 2 to ' the rate of oxidation was but little affected by the concentration

Now, Russell (J., 1926, 497) has shown that titanous sulphat 4*N*-sulphuric acid is very resistant to atmospheric oxidation, that even vanadous sulphate in 10*N*-sulphuric acid in a burett not measurably oxidised by air within an hour. It seemed p: able, therefore, that comparable concentrations of sulphuric : might exert a powerful retarding effect upon the oxidation of fer sulphate solutions. In view of the wide use of ferrous sulphate standardising permanganate solutions, it was decided to investi; these points more closely.

FIG. 1.



EXPERIMENTAL.

Influence of Concentration of Sulphuric Acid.—A slow curren purified air, saturated with moisture, was drawn through a serie flasks containing acid solutions of ferrous sulphate kept in a the ostat. At the conclusion of each run, the unoxidised ferrous sulpl was determined by titration with permanganate.* A few typ results are as follows :

Conc. of $FeSO_4$.	Temp.	Period of aspiration (hours).	Percentage oxidation of ferrous sulphate sulphuric acid of concentration: *N*/10.	*N*/5.	*N*/2.	*N*.	2*N*.	4*N*.	8.
N/25	60°	33	3·22	2·50	2·32	2·11	1·59	1·63	·
N/10	60	33	6·80	5·80	5·19	3·79	2·81	2·79	·
N/10	80	33	22·86	17·97	15·01	9·79	7·94	7·68	7
N/2	40	100	—	—	25·72	23·80	20·91	20·88	2(

These results are shown in Fig. 1. At all the temperat: studied, increase in concentration of sulphuric acid up to 2*N* gre:

* In all experiments a few drops of manganous sulphate solution ' added prior to titration.

increased the resistance to oxidation; beyond this point, however, further increase in acid had but little effect. If the function of the sulphuric acid were merely to reduce ionisation of the ferrous salt, one would expect, in accordance with the theory of Ennos, an increased oxidation on addition of the acid.

It would appear, therefore, that some complex is formed in solution which is more resistant to oxidation than un-ionised ferrous sulphate alone.

The increased oxidation with rise of temperature is clearly indicated and is in harmony with previous work.

Influence of Concentration of Ferrous Sulphate.—The foregoing results appear to indicate also that the percentage oxidation rises with the concentration of the ferrous sulphate, as noted by McBain (*loc. cit.*). In view of the contrary statement of Reedy and Machin (*loc. cit.*), however, it seemed desirable to confirm this, since any two of the preceding series may not be strictly comparable owing to the difficulty of ensuring exactly the same conditions of aspiration in two sets of tests. Further experiments were therefore carried out in which air was drawn through flasks containing solutions of ferrous sulphate of various concentrations in N-sulphuric acid at 40°. The results were as follows:

Period of aspiration (hours).	Percentage oxidation in ferrous sulphate solution of concentration:			
	$N/3$.	$N/5$.	$N/10$.	$N/25$.
50	12·03	7·67	3·84	2·24
30	7·14	4·55	2·18	0·44

The percentage oxidation is seen to be approximately proportional to the concentration, the oxidation–concentration curve being only slightly concave to the concentration axis. This supports the view (Ennos, *loc. cit.*) that the reaction is bimolecular at temperatures above atmospheric.

The optimum conditions for stability of ferrous sulphate solutions are thus high dilution, low temperature, and acidity of at least $2N$.

Preparation of Standard Solutions.—McBain concluded that, since dilute solutions of ferrous sulphate manifest relatively high stability, it should be unnecessary, when preparing standard solutions by dissolving iron in sulphuric acid, to observe the classical precaution of allowing the exit tube from the dissolving-flask to dip into sodium carbonate solution in order to prevent inrush of air during cooling. In two experiments he showed that, upon dissolving 1·4 g. of iron wire in 75 c.c. of $3N$-sulphuric acid over the Bunsen flame under continuous aëration, finally cooling rapidly and diluting to 250 c.c., the $N/10$-ferrous sulphate solution thus obtained contained only

0·04—0·05% of ferric iron, an amount usually negligible in ordinary volumetric analysis.

In view of the rapid increase in the rate of oxidation with rise of iron concentration, these results can only be taken, without further data, to apply to the particular concentrations used by McBain. The subject does not appear to have been further investigated, and the use of the carbonate trap is still recommended in modern text-books (see Bassett, "The Theory of Quantitative Analysis," 1925, p. 276).

In order to ascertain the limits within which no special precautions to avoid oxidation need be taken, the following experiments were carried out. Weighed pieces of iron wire were put into each of several series of round-bottomed flasks of *ca.* 500 c.c. capacity containing 100—200 c.c. of 4*N*-sulphuric acid, and warmed on the water-bath. The first flask in each series was fitted with a carbonate trap; the others were fitted with vertical tubes through rubber bungs, the tubes being some 20″ in length and of 0·2″ internal diameter. These functioned mainly as air condensers to prevent mechanical loss of solution with the escaping hydrogen, but also assisted to retain an atmosphere of hydrogen within the flask. Immediately the iron had completely dissolved, the flasks were rapidly cooled by immersion in a tank of cold water with gentle agitation but avoiding bubble formation. The contents of each flask were then made up to 250 c.c.,* the suspended carbon allowed to settle—a necessary precaution—and 25 c.c. titrated with permanganate. The results obtained in three selected series are given below, each titration representing the mean of several agreeing to within 0·03 c.c.

Initial vol. of acid.	200 c.c.	200 c.c.	100 c.c.†
Fe (g.) in 250 c.c.‡	4·3	1·4	1·0
Conc. of $KMnO_4$	*N*/3	*N*/10	*N*/10
	C.c. $KMnO_4$ per 0·43 g. Fe.	C.c. $KMnO_4$ per 0·14 g. Fe.	C.c. $KMnO_4$ per 0·1 g. Fe.
With carbonate trap	23·54	25·20	18·10
With vertical tube	23·57	25·22	18·09

† 6*N*-Sulphuric acid.

‡ In all the tests pure Armco iron wire was used. For analysis, see p. 3232.

The results clearly justify the omission of the carbonate trap when a vertical tube is used, provided that (i) the flask is removed from the water-bath immediately the iron has dissolved, and rapidly cooled in cold water, and (ii) the initial concentration of the sulphuric acid is sufficiently high to exceed 2*N* after the iron has dissolved. The former condition entails constant supervision of the experiment, which may be more trouble than the use of the carbonate trap.

* Recently-boiled distilled water was used in the experiment with the carbonate trap and ordinary distilled water in those with the vertical tube.

Experiments were therefore carried out to determine if rigid adherence to that condition is necessary. Approximately 1·4 g. of iron were dissolved in 150 c.c. of 4N-sulphuric acid under various conditions, and the solutions made up to 250 c.c. (see footnote, p. 3230); 25 c.c. were titrated with approximately N/10-permanganate with the following results (means of two titrations agreeing to 0·02 c.c.), calculated for exactly 1·400 g. of iron.

			$KMnO_4$, c.c.
1.	Carbonate trap		25·69
2.	Vertical tube.	Flask removed immediately iron dissolved, and rapidly cooled	25·72
3.	Do.	Flask removed immediately iron dissolved, and cooled slowly in air	25·65
4.	Do.	Flask kept 20 mins. on water-bath after iron had dissolved; then rapidly cooled	25·71
5.	Do.	Flask kept 20 mins. on water-bath after iron had dissolved; cooled slowly in air	25·69
6.	Do.	Flask kept 40 mins. on water-bath after iron had dissolved; cooled slowly in air	25·63

These results agree to within 0·4%, which is frequently sufficient for ordinary works practice. The best results are obtained by rapid cooling upon removal from the water-bath, whilst a few minutes extra on the bath after the iron has dissolved do not appreciably influence the result (Expts. 2 and 4).

In almost every case the vertical-tube method, as carried out in Expt. 2, yielded a slightly higher result (*ca.* 0·1%) than the carbonate-trap method. This would have been attributed to experimental error had it not occurred so persistently. Possibly it was due to traces of dissolved oxygen in the carbonate trap for, as shown below, the results obtained by the vertical-tube method are probably most correct, since they agree very closely with those obtained with sodium oxalate. Experiments with appreciably higher concentrations of ferrous sulphate, *viz.*, N/5 upwards, diverged appreciably from the standard under conditions 3, 5, and 6 above. This was to be expected in view of the increased rate of oxidation with rise in concentration. As such concentrations are less frequently used in practice the subject was not pursued further, but the results on p. 3230 show that excellent results are obtainable with even N/3 solutions by use of the vertical-tube method, provided that the precautions mentioned are duly observed.

The vertical-tube method of preparing N/10-ferrous sulphate solution has been found very useful in our laboratory. It is often more convenient than others because variations in temperature and acidity at the moment of titration do not affect the accuracy (Kolthoff, *Pharm. Weekblad*, 1924, **61**, 1082), whereas ferrous ammonium sulphate crystals vary slightly in composition (Hackl, *Chem. Ztg.*, 1922, **46**, 1065), and the temperature of sodium oxalate requires

regulating (Schröder, *Z. öffentl. Chem.*, 1910, **16**, 270, 290; Kolthoff, *loc. cit.*, p. 561). The last two methods, however, may be made to yield very accurate results agreeing to about 0·05% (McBride, *J. Amer. Chem. Soc.*, 1912, **34**, 393; Kolthoff, *Z. anal. Chem.*, 1924, **64**, 255; Hendel, *ibid.*, 1923, **63**, 321) if suitable precautions are taken. It was thus desirable to ascertain if these methods yielded results identical with the present one, as this does not appear to have been determined hitherto with accuracy. One difficulty is that for accurate work it is, of course, necessary to determine with proportionate exactness the composition of the iron used. This may be less convenient than the preparation of pure oxalates or ferrous salts. Electrolytic iron is frequently recommended, although even such metal is liable to contain appreciable amounts of impurity. A few parallel experiments have been carried out with sodium oxalate and Armco iron wire, the composition of which was as follows: C, 0·025; Si, 0·009; S, 0·033; P, 0·009; Mn, 0·036; Cu, 0·036; Fe (by difference) 99·852%. *N*/10-Solutions of permanganate, sodium oxalate, and ferrous sulphate were prepared, the last-named by dissolving 1·4 g. of iron wire in 200 c.c. of 4*N*-sulphuric acid on the water-bath, using the vertical tube, rapidly cooling in a tank of cold water and making up to 250 c.c. The permanganate was then standardised by titration with each of the above solutions. In titrating the sodium oxalate, the precautions mentioned by Schröder (*loc. cit.*) were carefully observed.

The following factors for two approximately *N*/10-permanganate solutions were obtained in two sets of experiments: with oxalate, (1) 0·9915, (2) 0·9878; with iron, (1) 0·9916, (2) 0·9866. Provided, therefore, that the composition of the iron is accurately known, this method of standardising permanganate agrees to within about 0·1% with that by sodium oxalate for *N*/10-solutions.

Conclusion.

In preparing standard solutions of ferrous sulphate by dissolving iron in sulphuric acid, a carbonate trap is not necessary. Very accurate results are obtainable when 150—200 c.c. of 4*N*-sulphuric acid and up to 1·4 g. of iron are warmed in a flask, fitted with a vertical tube, on the water-bath, and, immediately the iron has dissolved, rapidly cooled in water, and made up to a minimum of 250 c.c. Provided that the composition of the iron is accurately known, the result of standardising permanganate with such a solution agrees to within 0·1% with the sodium oxalate method.

THE TECHNICAL COLLEGE, BIRMINGHAM. [*Received, October 18th, 1928.*]

CCCCXXIX.—*Note on the Rate of Photochemical Combination of Chlorine and Hydrogen in Glass Capillary Tubes.*

By David Leonard Chapman and Philip Powell Grigg.

Determinations were recently made by Briers and Chapman (this vol., p. 1802) of the rates of photochemical union of bromine and hydrogen when the illumination of the mixture was intermittent, and it was shown that the results obtained could be interpreted by the assumption that the union of the gases is due to a catalyst formed by the light, and having an average life of an appreciable fraction of a second. As the results of the measurements of the rates of chemical change can in general be explained by more than one set of hypotheses, it is desirable that evidence, if possible of a different character, should be obtained of such long-lived catalysts in other cases of photochemical change. The experimental method adopted in the case of bromine and hydrogen cannot be applied, as already explained (*loc. cit.*), in the case of chlorine and hydrogen. However, there is another simple method of testing whether a similar theory is applicable to the photochemical union of the latter gases.

If we postulate that the union of chlorine and hydrogen is due to an unstable catalyst, and that the catalyst is destroyed when it comes into contact with glass or a film of water, then obviously if the catalyst has an appreciable life it ought to be possible to show that in light of the same intensity the rate of union of chlorine and hydrogen in capillary tubes is less than in tubes of wider diameter. The experiment has been performed and has furnished a positive result.

The determinations were made with a hermetically sealed glass apparatus of the form of a U-tube of which one limb was a capillary tube of 1 mm. internal diameter, and the other limb a tube of about 2·5 cm. diameter. The apparatus contained about 3 c.c. of water and electrolytic gas at atmospheric pressure. In purifying the water and in preparing the electrolytic gas, the usual precautions were taken to eliminate destructible inhibitors. Furthermore, as an additional precaution, the apparatus, after it had been filled and sealed, was heated at 130° for 6 hours in a bath of glycerol.

The preliminary experiments were performed in the following manner. The previously filled apparatus was placed in a horizontal position and the water removed from the capillary tube by heating it with steam. Then, in order to be certain that the capillary tube contained gas of the same composition as that in rest of the apparatus, the former was warmed and cooled many times. The apparatus was

next fixed in a vertical position so that the water enclosed the gas in the capillary tube, which was then warmed so as to drive out about one-fourth of the gas it contained. The water which moved up the capillary tube on its regaining the temperature of the laboratory served as an index.

When the whole apparatus was exposed to light, so that both tubes were equally illuminated, the index in the capillary tube moved downwards, showing that the rate of combination of the gases in the wider tube was more rapid than that of the gases enclosed in the capillary. After exposure to light and before the final reading of the index was taken, the apparatus was allowed to stand at a constant temperature in the dark for 12 hours to ensure the attainment of complete equilibrium. Then, in order to estimate the proportions of hydrogen chloride formed in the wide and narrow tubes, the apparatus was completely immersed in water in an upright position, and the sealed end of the wide tube opened. The water which immediately entered the wider tube filled from one-third to one-half of its volume, showing that a considerable proportion of the gases originally contained therein had combined. The index in the capillary tube, however, only rose to its initial position, thereby showing—since the pressure of the gas in the capillary tube was initially and finally approximately the same, namely, that of the atmosphere—that only a small proportion of the gases introduced into it had united.

To measure more accurately the relative rates of combination in the two tubes, the capillary tube alone and the wider tube alone were alternately exposed to light of the same intensity. The downward movement of the index which accompanied the exposure of the wider tube to light was 40—60 times more rapid than the upward movement of the index resulting from the illumination of the capillary tube alone. Before the readings were taken, sufficient time was always allowed to elapse to ensure complete solution of the hydrogen chloride formed, and a correction was applied for the light totally reflected from the sides of the bore of the capillary tube. That the ratios of the rates of combination observed in different experiments were not constant was to be expected, since electrolytic gas contains varying small proportions of oxygen, which, being an inhibitor, would shorten the life of the catalyst.

The precautions taken to destroy destructible inhibitors appear to us to exclude the possibility that the observed effect was due to the gradual escape of such inhibitors from the surface of the glass. Moreover, the possibility that the rate of union of the chlorine and hydrogen in the capillary tube was inhibited by hydrochloric acid is excluded by well-known experiments of Bodenstein.

From the above-described phenomenon, an attempt will be made, with an apparatus designed for the purpose, to obtain an estimate of the life of the catalyst.

Jesus College, Oxford. *[Received, October 23rd, 1928.]*

CCCCXXX.—*Crystallography of the Aliphatic Dicarboxylic Acids.*

By William Augustus Caspari.

The straight-chain saturated acids of this series, besides being all solid at the ordinary temperature, lend themselves better to crystallographic study than the corresponding monocarboxylic acids, in that their crystals are harder and less liable to distortion. An advantage, moreover, of dealing with acids of comparatively low molecular weight is that crystals can be procured which have a reasonable thickness in the direction of the *c* axis instead of being excessively thin and tabular.

Angle measurements on crystals of the lower members of the series, up to pimelic acid (C_7) have been made by various workers. From C_4 onwards they all crystallise in the monoclinic–prismatic class. The results of an *X*-ray examination of succinic acid (C_4) have been published by Yardley (*Proc. Roy. Soc.*, 1924, *A*, **105**, 451). A number of data bearing on the spacings of the basal planes, obtained by *X*-ray powder photographs and carried up to C_{34}, are due to Normand, Ross, and Henderson (J., 1926, 2632; *Proc. Roy. Soc. Edin.*, 1928, **48**, 20). It is assumed by the latter workers, and is now amply confirmed, that the length of the unit cells of these crystals, along *c*, depends on the number of carbon atoms in the molecule, as established by Shearer and Müller for other long-chain componnds.

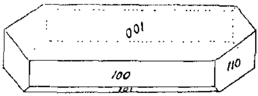
The acids available in the form of single crystals for the present examination were adipic (C_6), pimelic (C_7), suberic (C_8), azelaic (C_9), sebacic (C_{10}), brassylic (C_{13}), and hexadecanedicarboxylic (C_{18}). For obtaining crystals of adequate quality, ethyl acetate was found in most cases to be the best solvent. With all the acids, cooling of hot aqueous solutions leads to crystals which are well-shaped except for extreme thinness upon (001), whereby they are rendered useless; but pimelic acid crystallises best by isothermal evaporation from water, in which it is moderately easily soluble in the cold. For sebacic acid, cooling of warm solutions in concentrated nitric acid gave the best results. Good crystals of suberic acid were not obtained until the method was adopted of heating

the substance with ether in sealed tubes to about 100° and allowing it to cool in the oven.

Externally, the crystals of all the acids conform to the same type, with variations in face-development due to impurities and to the kind of solvent employed. The principal forms are always (001), (100), and (110), with, occasionally, (10$\bar{1}$) and (010). On pimelic acid crystals, (011) was also observed. Throughout the series, (001), (100), and (110) are pronounced cleavage-planes. The crystals are tabular upon (001) and become progressively thinner as the molecular weight rises. The majority of them are elongated along the *b* axis, so that on the whole the characteristic habit is that shown in Fig. 1. The β-angle is unusually large, varying from 128° to 137°. Swallow-tail twins about (001), with the *b* axes aligned, are common, and crossed twins about (001), with the *b* axes at right angles, also occur.

In the lower members of the series (101) is almost as well developed as (100), and earlier observers have sometimes chosen the former as containing the *c* axis, thus reducing β to the neighbourhood of 90°. As one ascends the series, however, the crystals seldom or never display the nearly orthogonal (101) face, whilst the highly tilted (100) face is always in evidence, besides being a definite cleavage-plane. The large β-angle therefore appears to be a reality. Angles lying in the same region of magnitude have been observed by Müller (*Proc. Roy. Soc.*, 1927, *A*, **114**, 542) in bromostearic, stearolic, and behenolic acids.

Fig. 1.



The β-angle of adipic acid (Brugnatelli, *Z. Kryst.*, 1896, **26**, 298) is known from earlier measurements. Those of the other acids concerned were now determined goniometrically. Whereas reflexions from (001) were uniformly good, those from (100) were less satisfactory, owing to the narrowness of the face and its tendency to unevenness. It was therefore considered advisable to select the results of the best reflexions from several crystals and to state the mean to the nearest 10′. The angles so found agree, within the experimental limits, with those which may be independently calculated from the *X*-ray spacings of the (001) and (100) planes.

The crystals were subjected to *X*-ray analysis by means of rotation photographs of single crystals about their three axes, upon glass quarter-plates. When required for closer investigation of particular reflexions, oscillation photographs were also taken. The

β-angles and cell-dimensions (in Å.U.) of the several crystals are summarised in Table I.

TABLE I.

Acid.	a.	b.	c.	β.	Mols. in cell.
C_6, Adipic	10·27	5·16	10·02	137° 5′	2
C_7, Pimelic	9·93	4·82	22·12	130° 40′	4
C_8, Suberic	10·12	5·06	12·58	135° 0′	2
C_9, Azelaic	9·72	4·83	27·14	129° 30′	4
C_{10}, Sebacic	10·05	4·96	15·02	133° 50′	2
C_{13}, Brassylic	9·63	4·82	37·95	128° 20′	4
C_{18}, Hexadecanedicarboxylic	9·76	4·92	25·10	131° 10′	2

The first point of interest which is brought out by these figures is that the unit cells of all the acids have about the same breadth and depth. From this alone it necessarily follows that the carbon-atom chain of the structural molecule must be strung out along the *c* axis.

As regards the *c* dimensions of the several unit cells, it is seen that the crystals fall into two groups, according to the odd or even number of carbon atoms in the molecule. The *c* axes of the even-carbon series are nearly proportional to the number of carbon atoms, whilst in the odd-carbon series they are proportional to twice that number. In the latter series the heights of the cells are doubled and must be taken up by two molecules end to end; correspondingly the cells contain the substance of four instead of two molecules.

This difference in crystal structure between even-carbon and odd-carbon acids cannot be unconnected with the well-known alternation in their melting points. Ultimately the melting point must depend on the ease with which molecules are torn out of the crystal lattice, and it is plausible to suppose that the double cells of the odd-carbon acids (having relatively lower m. p.'s) are less stable in this respect than the more compact cells of the even-carbon acids. A full explanation, however, must be deferred until not only the exact structures of the crystals but also the degree of molecular association in the molten substances are better known.

An alternation in most of the data in Table I is apparent as the homologous series is ascended, and is especially striking with the β-angles, which are always considerably smaller for odd-carbon than for even-carbon acids. The gentle alternation in the *a* and *b* cell-dimensions shows a tendency to die out as the molecular weight rises.

With each crystal, reflexions from planes to the number of 30—50 were identified upon the photographs. Owing to the close similarity of all the *a* and *b* axial lengths, the rotation photographs about these respective axes were much alike among themselves, whilst the *c* axis photographs varied characteristically with the crystal. Reflexions from (110) and (200) were very strong through-

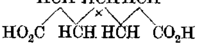
out, and (211) fairly strong. In the even-carbon series, (210), which did not appear at all in the odd-carbon series, was also fairly strong. On the other hand, (011) appeared intensely in the latter but only faintly or not at all in the former series; this confirms the structures in Fig. 2, where (011) planes in the odd-carbon series are seen to have a greater reticular density than (011) planes in the even-carbon series.

Orders of (001) attained at most only moderate intensity and were represented by both odd and even orders, beginning with (001), in the even-carbon acids, but by even orders only, beginning with (002), in the odd-carbon acids. By a simple application of the structure factor of intensity, this disappearance of the odd orders indicates a division of the unit cell across c into halves of nearly equivalent reflecting power, and is what would be expected from the structure (Fig. 2) of odd-carbon acids. A minor subdivision of the c heights is caused by successive layers of the carbon atoms themselves in the plane of (001). The effect of this, again by operation of the structure factor, is well brought out in the c axis photographs, where remote hyperbolas (layer-lines) show a certain intensity after an interval of weak or unrepresented hyperbolas. Thus, in adipic acid the 3rd and 4th hyperbolas are relatively strong, in suberic the 4th and 5th, in sebacic the 6th, and in the C_{18} acid the 8th and 9th. In pimelic acid the 8th hyperbola emerges strongly, in azelaic the 10th, and in brassylic the 14th.

On scrutinising all the planes represented by X-ray reflexions, it was found that in no case is there a general halving in the (hkl) series; hence the space-lattice is the simple lattice Γ_m. On the other hand, such planes as (100), (101), (300), etc., did not appear, but (200), (205), (402), etc., were frequent; that is, $(h0l)$ is halved when h is odd. Lastly, since (020) appears but never (010), we may conclude that the space-group is C_{2h}^5.

If the molecule is asymmetrical, four differently oriented molecules must constitute a unit cell. Such is the case with odd-carbon acids; their molecules therefore must be without symmetry. In the case of even-carbon acids there are only two in the cell, and the molecule must have a centre of symmetry of its own which it contributes to the symmetry of the cell. From the structural formulæ, it is easily seen how the one series of acids can have central symmetry and the other none, thus:

Odd :—



Even :—

Any straight line drawn through the centre of symmetry at × cuts equivalent atoms or groupings at opposite boundaries of the molecule when the carbon-atom number is even, but not when it is odd. Similar considerations apply, for example, to hydrocarbons; and, indeed, it is found by Müller (*loc. cit.*) that octadecane, $C_{18}H_{38}$, has two molecules to the cell, but $C_{29}H_{60}$ has four. All monocarboxylic acid molecules may be expected to be asymmetrical and to form four-molecule cells.

Some further points of similarity and contrast between the several acids may be gathered from Table II.

TABLE II.

Acid.	*d.*	*ab* sin β.	*D.*	Gap.
C_6, Adipic	1·340	36·18	—	3·70
C_7, Pimelic	1·313	36·26	—	3·47
C_8, Suberic	1·270	36·24	2·56	3·73
C_9, Azelaic	1·252	36·22	2·50	3·47
C_{10}, Sebacic	1·240	35·96	2·48	3·65
C_{13}, Brassylic	1·173	36·41	2·50	3·81
C_{18}, Hexadecanedicarboxylic	1·138	36·20	2·64	3·62
Mean		36·21	2·53	3·63

The densities are calculated by the relation $d = 1{\cdot}66MN/abc \sin \beta$, where M is the molecular weight and N the number of molecules in the unit cell. Values so found contain the errors of four separate experimental quantities, and are not precise enough to decide whether there is an alternation along the series; if there is, however, it can be but slight.

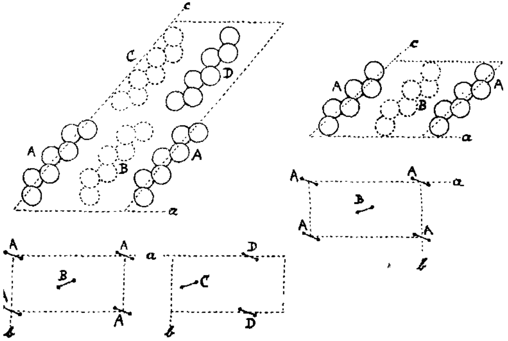
The quantity $ab \sin \beta \times 10^{-16}$ cm.^{2} expresses the area of a section of the unit cell taken, not along (001), but at right angles to the *c* axis, and is seen to be fairly constant. Moreover, all the long-chain aliphatic compounds hitherto examined, including bromostearic acid, show similar values for $ab \sin \beta$, ranging from 35·8 to $37{\cdot}8 \times 10^{-16}$ cm.^{2}. This remarkable uniformity leaves it hardly doubtful that all the crystals concerned are built up in the same way, *viz.*, of parallel bundles of carbon-atom chains along the *c* axis, with ample space between them to accommodate hydrogen, oxygen, and other atoms.

The lengths of the *c* axes in Table I would not permit a row of carbon atoms of diameter 1·54 Å.U. to lie with their centres in a straight line; these atoms must therefore lie in zigzag formation along the chain. The unit cells of adipic and pimelic acids, on this hypothesis, are shown diagrammatically in Fig. 2, with the (010) face or monoclinic plane of symmetry in the plane of the paper. The ground-plans of the corresponding (001) or basal sides of the cell are given underneath. The molecules are shown as flat zigzag

hains of carbon atoms, the angle of zigzag being not far from the etrahedral angle. There is as yet no evidence as to the arrangement of the methylenic hydrogen atoms or of the groups of hydrogen nd oxygen atoms which cluster at each extremity, and they are ot shown in the figure; in the case of even-carbon acids, however, ve know that all these atoms must be disposed in harmony with the entro-symmetry of the molecule.

Those molecules which lie half-way across the cell are drawn in otted lines. Molecules B, in the case of even-carbon acids, are so isposed as to lie symmetrically both across a glide-plane and about

FIG. 2.



Pimelic acid. *Adipic acid.*

screw-axis towards molecules A. In the odd-carbon cell, molecules are reflexions of A, molecules C are derived by rotation from A, nd molecules D are reflexions of C. The upper half of the cell is rovisionally shown slightly displaced against the lower half in the direction, on the analogy of the structure of $C_{29}H_{60}$ as worked out y Müller (*Proc. Roy. Soc.*, 1928 *A*, **120**, 437), hut space-group onsiderations alone afford no information as to this. The planes the zigzag chains will not lie exactly parallel to (010) or (100), ecause the central molecule B would then be almost identical with , in which case we should expect halvings of the (*hkl*) planes in the -ray spectra. In Fig. 2 the projections of the molecules upon e base are shown inclined at an undetermined angle, which angle, its symmetrical counterpart, must be the same for all molecules.

The available data enable us to calculate the distance (*D*) between

successive carbon atoms on any one side of the chain—the wave-length, as it were, of the zigzag. By subtracting $2c$ of each even-carbon acid from $2c$ of adipic acid, and c of odd-carbon acids from c of pimelic acid, and dividing by the difference in the number of carbon atoms in the molecules, we obtain the required distances, which are stated in col. 3 of Table II. Although the results are only roughly constant, they point to a uniform mean distance, between centres of carbon atoms, of 2·53 Å.U. Here again there is striking agreement with other crystal structures. For diamond, the corresponding distance is 2·52 Å.U., whilst for the hydrocarbon $C_{29}H_{60}$ it has been evaluated (Müller, *loc. cit.*, 1928) as 2·537 Å.U.

Lastly, it is clear that in each crystal there must be a gap between successive molecules, measured in the line of the c axis, since the quotient c/n decreases as the molecules grow longer. This gap, as between centres of terminal carbon atoms, is found by calculating $c - 2{\cdot}53(n-1)/2$ or $c/2 - 2{\cdot}53(n-1)/2$, and the results are given in the fourth column. If the diameter of the carbon atom be assumed to be 1·54 Å.U., the mean gap of 3·63 Å.U. between centres corresponds to a clear gap of 2·09 Å.U., to the filling of which the oxygen and hydrogen atoms of two carboxyl groups must contribute. The extent of the gap is somewhat larger than that found for $C_{29}H_{60}$, *viz.*, 3·09 Å.U. between centres, as might be expected when the molecule has carboxyl groups at each end.

The author desires to express his indebtedness to Prof. J. F. Thorpe, F.R.S., and to Mr. N. K. Adam for courteous gifts of specimens, and to Sir William Bragg, F.R.S., for the interest he has taken in this work.

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THE ROYAL INSTITUTION. [*Received, October 24th,* 1928.]

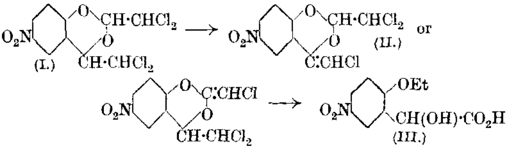
CCCCXXXI.—*The Condensation of Dichloroacetaldehyde with Phenols.*

By FREDERICK DANIEL CHATTAWAY and ALEXANDER ALLAN MORRIS.

THE new type of condensation between phenols and aldehydes leading to the formation of the dioxin ring (J., 1926, 2720; 1927, 385, 2013; this vol., p. 1088) is not confined to chloral, but appears to be a general reaction of those aldehydes which can be kept in contact with concentrated sulphuric acid for some time without decomposition. Dichloroacetaldehyde, for example, reacts with p-nitrophenol and phenol-p-sulphonic acid even more readily than chloral itself.

Thus with *p*-nitrophenol two molecules of the aldehyde condense with loss of one molecule of water, the final product being 6-*nitro*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin* (I). No hydroxyl group is present in the molecule, since the compound does not dissolve in dilute alkali solution and can be recrystallised unchanged from boiling acetic anhydride. It contains the nitro-group unchanged, since this can be reduced to an amino-group which can be acetylated or diazotised and replaced, the dioxin ring remaining unbroken during these reactions.

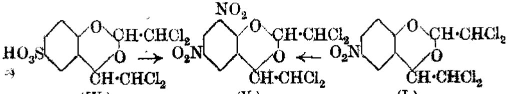
When the benzdioxin (I) is acted upon by alcoholic potash at 50—60°, one molecule of hydrogen chloride is removed from one of the $\cdot CH\cdot CHCl_2$ groups with formation of 6-*nitro*-2(or 4)-*dichloromethyl*-4(or 2)-*chloromethylene*-1 : 3-*benzdioxin* (II). If the temperature is not controlled, reaction proceeds further with the formation of 5-nitro-2-ethoxymandelic acid (III) as the final product, a reaction which establishes the constitution of the compound.


(I.) (II.) (III.)

Similarly, dichloroacetaldehyde condenses with phenol-*p*-sulphonic acid, yielding 2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin*-6-*sulphonic acid* (IV). This compound behaves as a normal sulphonic acid. It is a colourless solid with no definite melting point and crystallises with one molecule of water. This molecule of water is probably attached to the sulphonic residue, since the ammonium salt is obtained in the anhydrous condition.

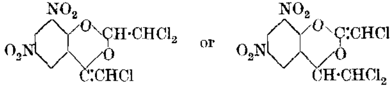
When acted upon by phosphorus pentachloride, the sulphonic acid yields a *sulphonyl chloride*. This with methyl and ethyl alcohols yields *esters*, with ammonia a *sulphonamide*, and with aniline a *sulphonanilide*.

The constitution of the sulphonic acid is similar to that of the condensation product (I), yielded by *p*-nitrophenol and dichloroacetaldehyde, since both compounds on nitration yield 6 : 8-*dinitro*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin* (V).


(IV.) (V.) (I.)

When acted upon by alcoholic potash, the dinitro-compound (V) loses one molecule of hydrogen chloride with formation of 6 : 8-*dinitro*-2(or 4)-*dichloromethyl*-4(or 2)-*chloromethylene*-1 : 3-*benzdioxin* (VI).

(V.) ⟶ (VI.)



The further action of alcoholic potash causes profound decomposition.

EXPERIMENTAL.

6-Nitro-2 : 4-bisdichloromethyl-1 : 3-benzdioxin (I).—Dichloroacetaldehyde alcoholate (70 g.; 2 mols.) was added slowly with shaking to a well-cooled solution of *p*-nitrophenol (30 g.; 1 mol.) in 300 c.c. of concentrated sulphuric acid. The solution became warm and fumes of hydrogen chloride were given off while a viscid, yellow solid slowly separated on the surface. The mixture was kept at the ordinary temperature for 4 hours with occasional shaking and then poured over crushed ice. The viscid, brown solid obtained was freed from sulphuric acid by repeated washing with hot water and dissolved in boiling alcohol, in which it was readily soluble. On cooling, 6-*nitro*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin* separated. It was freed from a little unchanged *p*-nitrophenol by washing with warm dilute ammonia and hot water and recrystallised several times from boiling alcohol, in which it was very soluble, separating in pale yellow, flattened, rhombohedral plates (23 g.), m. p. 113·5° (Found : C, 35·0; H, 2·1; N, 4·1; Cl, 41·2; *M*, cryoscopic in benzene, 352, 357. $C_{10}H_7O_4NCl_4$ requires C, 34·6; H, 2·0; N, 4·0; Cl, 40·9%; *M*, 347).

6-Nitro-2(or 4)-dichloromethyl-4(or 2)-chloromethylene-1 : 3-benzdioxin (II).—6-Nitro-2 : 4-bisdichloromethyl-1 : 3-benzdioxin (20 g.; 1 mol.) was gradually added to a solution of potassium hydroxide (24 g.; 7 mols.) in 250 c.c. of alcohol kept at 50—60° by frequent cooling. The dark brown solution was then nearly neutralised with hydrochloric acid, the alcohol distilled off in steam, and the viscid, brown residue crystallised several times from alcohol and finally from chloroform–light petroleum. The 6-*nitro*-2(or 4)-*dichloromethyl*-4(or 2)-*chloromethylene*-1 : 3-*benzdioxin* thus obtained separated from boiling alcohol, in which it was easily soluble, in slender, very pale yellow prisms, m. p. 108° (Found : C, 38·9; H, 2·0; N, 4·7; Cl, 34·2. $C_{10}H_6O_4NCl_3$ requires C, 38·6; H, 1·9; N, 4·5; Cl, 34·3%). Although apparently unsaturated, the compound does not form an addition product with bromine.

5-Nitro-2-ethoxymandelic Acid (III).—A vigorous reaction took place when 25 g. (1 mol.) of the nitro-compound (I) were added gradually to a hot solution of 30 g. (7 mols.) of potassium hydroxide in 250 c.c. of alcohol, the temperature rising and the solution darkening. The solution was gently boiled for 15 minutes and then nearly neutralised with hydrochloric acid and the alcohol was distilled off in steam. From the filtered solution, strongly acidified with hydrochloric acid, ether extracted 5-nitro-2-ethoxymandelic acid (5 g.), m. p. 138° after crystallising from hot water (compare Chattaway, J., 1926, 2724) (Found: C, 49·7; H, 4·65; N, 5·8. Calc. for $C_{10}H_{11}O_6N$: C, 49·8; H, 4·6; N, 5·8%). The acetyl derivative formed rhombic plates, m. p. 147° (compare Chattaway, *loc. cit.*).

6-Amino-2 : 4-bisdichloromethyl-1 : 3-benzdioxin.—Iron filings (15 g.; 3 mols.) were added in small quantities to a hot solution of 30 g. (1 mol.) of the nitro-compound (I) in 250 c.c. of alcohol containing 66 c.c. (7 mols.) of 33% hydrochloric acid. The hot green solution was filtered, the alcohol removed partly by distillation and finally by evaporation on the water-bath, 100 c.c. of cold water were added to the solid residue to dissolve the iron salts, and on filtration the *hydrochloride* of 6-amino-2 : 4-bisdichloromethyl-1 : 3-benzdioxin was left as a crystalline mass of small, colourless prisms (30 g.). After recrystallisation from boiling dilute hydrochloric acid, in which it was easily soluble, it melted and decomposed at about 210° (Found: Cl, 50·1. $C_{10}H_9O_2NCl_4$,HCl requires Cl, 50·2%).

On warming the hydrochloride with a dilute solution of sodium carbonate, *6-amino-2 : 4-bisdichloromethyl-1 : 3-benzdioxin* was liberated as a colourless solid, readily soluble in boiling dilute alcohol, from which it separated in thin, colourless, lustrous plates, m. p. 108·5—109·5° (Found: Cl, 44·8. $C_{10}H_9O_2NCl_4$ requires Cl, 44·75%).

6-Acetamido-2 : 4-bisdichloromethyl-1 : 3-benzdioxin was formed with evolution of heat when the base was heated for a few minutes with acetic anhydride (slightly more than 1 equiv.), and the *6-diacetamido*-derivative was formed when the base (2 g.) was boiled for 5 minutes with acetic anhydride (10 c.c.) and one drop of concentrated sulphuric acid. They separated from boiling dilute alcohol, the former in small compact prisms, m. p. 149—150° (Found: Cl, 39·5. $C_{12}H_{11}O_3NCl_4$ requires Cl, 39·5%), and the latter in small plates, m. p. 145° (Found: Cl, 35·35. $C_{14}H_{13}O_4NCl_4$ requires Cl, 35·4%).

A solution of 2 : 4-bisdichloromethyl-1 : 3-benzdioxin-6-diazonium chloride was formed when nitrous fumes were passed into a solution of 15 g. of the preceding hydrochloride in 50 c.c. of alcohol, through which a little dry hydrogen chloride had been passed, cooled to −6°. On addition of bromine dissolved in a saturated solution of potassium

bromide, 2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin*-6-*diazonium perbromide* separated as a canary-yellow solid. The perbromide is remarkably stable and crystallises unchanged from warm acetic acid, containing a little free bromine, in small, compact, orange prisms which decompose with brisk evolution of bromine at 128—129° (Found: Cl + Br, 67·1. $C_{10}H_7O_2N_2Cl_4Br_3$ requires Cl + Br, 67·1%).

When boiled for some time with acetic acid, the perbromide decomposes with evolution of bromine, and from the concentrated cooled solution, 6-*bromo*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin* separates in small, colourless, lustrous plates, m. p. 91·5° (Found: Cl + Br, 58·1. $C_{10}H_7O_2Cl_4Br$ requires Cl + Br, 58·2%).

2 : 4-*Bisdichloromethyl*-1 : 3-*benzdioxin*-6-*sulphonic Acid* (IV).—To a well-cooled solution of 30 g. of phenol (1 mol.) in 300 c.c. of concentrated sulphuric acid, 102 g. of dichloroacetaldehyde alcoholate (2 mols.) were added slowly with stirring. After remaining at the ordinary temperature for 6 hours with occasional stirring, the mixture was poured over 150 g. of ice. The *sulphonic acid*, which separated as a white solid, was recrystallised from hot, dilute hydrochloric acid (yield, 40 g.), dried on the water-bath, and dissolved in boiling chloroform, in which it was only very moderately soluble; on addition of low-boiling petroleum it separated in minute, colourless prisms containing $1H_2O$, m. p. 150—155° (decomp.) (Found: C, 30·0; H, 2·5; S, 8·2; Cl, 35·6. $C_{10}H_8O_5Cl_4S,H_2O$ requires C, 30·0; H, 2·5; S, 8·0; Cl, 35·5%).

The monohydrated acid is very soluble in water, acetic acid, alcohol, and ether, and very sparingly soluble in benzene. When heated at 105—110°, it slowly decomposes. It forms an anhydrous *ammonium* salt, which separates from a dilute solution of ammonia in extremely small, colourless prisms (Found: N, 3·5; S, 8·4; Cl, 35·6. $C_{10}H_{11}O_5NCl_4S$ requires N, 3·5; S, 8·05; Cl, 35·55%).

6 : 8-*Dinitro*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin* (V).—To 20 g. of the monohydrated acid suspended in 40 c.c. of concentrated sulphuric acid, a mixture of 40 c.c. of nitric acid (*d* 1·5) and 40 c.c. of nitric acid (*d* 1·41) was added slowly with shaking. Heat was evolved and an emulsion of oily drops was formed. After vigorous shaking for 10 minutes the emulsion was poured into a mixture of ice and water; a semi-solid mass then separated which solidified on cooling. This was crushed and washed with warm water, dried on the water-bath, and dissolved in alcohol, in which it was easily soluble and from which it separated in small, compact, slightly yellow prisms, m. p. 133·5—134·5° (Found: N, 7·1; Cl, 36·2. $C_{10}H_6O_6N_2Cl_4$ requires N, 7·15; Cl, 36·2%).

6 : 8-*Dinitro*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin* identical with

the above compound in every way was obtained when 6-nitro-2 : 4-bisdichloromethyl-1 : 3-benzdioxin (I) was nitrated in the same manner. Unlike the analogously constituted 6 : 8-dinitro-2 : 4-bistrichloromethyl-1 : 3-benzdioxin (compare Chattaway and Morris, J., 1927, 2013), it does not form polymorphic modifications.

6 : 8-*Dinitro*-2-(or 4)-*dichloromethyl*-4(or 2)-*chloromethylene*-1 : 3-*benzdioxin* (VI).—Potassium hydroxide (1·5 g.; 1 mol.), dissolved in 10 c.c. of alcohol, was added to a hot solution of 10 g. of the preceding dinitro-compound (1 mol.) in 100 c.c. of alcohol. An immediate rose-red colour was developed which quickly changed to brown. The mixture was gently warmed on the water-bath for a few minutes, a little water added, and the alcohol distilled off in steam; a viscid, reddish-brown solid then separated. By repeated crystallisation from small quantities of alcohol, 6 : 8-*dinitro*-2(or 4)-*dichloromethyl*-4(or 2)-*chloromethylene*-1 : 3-*benzdioxin* was obtained in well-formed, yellow rhombohedra, m. p. 144° (Found: C, 34·3; H, 1·4; N, 7·95; Cl, 29·8. $C_{10}H_5O_6N_2Cl_3$ requires C, 33·8; H, 1·4; N, 7·9; Cl, 29·9%). Like 6-nitro-2(or 4)-dichloromethyl-4(or 2)-chloromethylene-1 : 3-benzdioxin (II), it does not form an addition product with bromine.

2 : 4-*Bisdichloromethyl*-1 : 3-*benzdioxin*-6-*sulphonyl Chloride*.—The monohydrated acid (24 g.) and powdered phosphorus pentachloride (50 g.) were mixed and warmed on a water-bath for a few minutes, a brown oil being formed. This was poured slowly over ice. The *sulphonyl chloride*, which separated as a colourless solid, was dissolved in ether, from which, on addition of low-boiling petroleum, it separated in small, lustrous, colourless prisms, m. p. 105—106° (Found: Cl, 43·85. $C_{10}H_7O_4Cl_5S$ requires Cl, 44·3%).

When boiled with any alcohol, it reacts readily and yields the corresponding alkyl sulphonate. *Methyl* 2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin*-6-*sulphonate* separates from boiling methyl alcohol in lustrous flattened prisms, m. p. 110—111·5° (Found: Cl, 36·0. $C_{11}H_{10}O_5Cl_4S$ requires Cl, 35·8%), and the *ethyl* ester from boiling ethyl alcohol in small, compact prisms, m. p. 148—149·5° (Found: Cl, 34·6. $C_{12}H_{12}O_5Cl_4S$ requires Cl, 34·6%).

The sulphonyl chloride also reacts readily with ammonia and with aniline in boiling alcohol to form the *sulphonamide* and the *sulphonanilide*, which separate from boiling dilute alcohol in small, silvery prisms, m. p. 175·5° (Found: Cl, 37·0. $C_{10}H_9O_4NCl_4S$ requires Cl, 37·2%), and in small, colourless prisms, m. p. 166—167° (Found: N, 3·15; Cl, 30·9. $C_{16}H_{13}O_4NCl_4S$ requires N, 3·1; Cl, 31·0%) respectively.

THE QUEEN'S COLLEGE, OXFORD. [*Received, November 5th, 1928.*]

CCCCXXXII.—*Preparation of Diethylaminoethanol Esters of Diphenyl-2-carboxylic Acid and Derivatives.*

By Frank Bell.

Roberts and Johnson (*J. Amer. Chem. Soc.*, 1925, **47**, 1399) have directed attention to the marked anæsthetic action of diethylaminoethyl diphenate, and it was thought of interest to make the diethylaminoethyl esters of several related carboxylic acids.

Diphenyl-2-carboxylyl chloride reacted with diethylaminoethyl alcohol to give an *ester hydrochloride* with a well-marked anæsthetic action. The chlorides of diphenyl-4-carboxylic, fluorenone-4-carboxylic, and 2′-cyanodiphenyl-2-carboxylic acids furnished esters of perceptible but smaller action. *2′-Cyanodiphenyl-2-carboxylyl chloride* was obtained together with about 10% of diphenimide by the action of thionyl chloride on diphenamic acid (compare the action of thionyl chloride on diphenic acid; J., 1927, 1698).

$$\begin{matrix} C_6H_4{\cdot}CO_2H \\ C_6H_4{\cdot}CO{\cdot}NH_2 \end{matrix} \longrightarrow \begin{matrix} C_6H_4{\cdot}COCl \\ C_6H_4{\cdot}CN \end{matrix} + \begin{matrix} C_6H_4{\cdot}CO \\ C_6H_4{\cdot}CO \end{matrix}\!\!>NH$$

Diphenyl-2-carboxylyl chloride shows a great tendency to change into fluorenone during distillation. On the other hand, diphenoyl dichloride seems quite stable, although its boiling point is almost 50° higher. 2′-Cyanodiphenyl-2-carboxylyl chloride decomposed to only a slight extent; the 4-cyanofluorenone produced was found in the distillate. The considerable stability of this acid chloride is of interest, because the convenient process for obtaining 4-cyanofluorenone by the action of phosphorus pentachloride on phenanthraquinone monoxime (Borsche and Gander, *Ber.*, 1914, **47**, 2818) must depend on its intermediate formation.

Experimental.

Diphenyl-2-carboxylyl chloride was obtained as a pale yellow liquid, b. p. 163°/10 mm., when a solution of diphenyl-2-carboxylic acid in warm thionyl chloride was distilled in a vacuum (Found: C, 72·0; H, 4·1. Calc.: C, 72·1; H, 4·2%) (compare Schlenk and Bergmann, *Annalen*, 1928, **464**, 33). In two subsequent experiments the chloride decomposed completely during distillation with the formation of pure fluorenone. Bretscher, Rule, and Spence (this vol., p. 1502) have apparently had the same experience and are investigating the reaction in detail.

Interaction of this chloride and 2-aminodiphenyl in pyridine solution gave the corresponding *amide*, which crystallised from acetic acid in needles, m. p. 194° (Found: C, 85·5; H, 5·5. $C_{25}H_{19}ON$ requires C, 85·9; H, 5·4%).

Diethylaminoethyl Diphenyl-2-carboxylate.—Diethylaminoethyl alcohol (5 g.) was added to a solution of the acid chloride (9·2 g.) in benzene (20 c.c.). The semi-solid product was warmed on the water-bath for ½ hour and evaporated in a vacuum, and the residual gum dissolved in cold water. The base was liberated with ammonia, extracted with ether, and distilled in a vacuum, giving a colourless liquid, b. p. 183°/1 mm., which contained some impurity (Found: C, 75·9; H, 7·6. $C_{19}H_{23}O_2N$ requires C, 76·8; H, 7·8%). It was treated in dry ether with hydrogen chloride (slightly less than the theoretical amount), the *hydrochloride of* diethylaminoethyl diphenyl-2-carboxylate being precipitated as a white powder, m. p. 109—110° (Found: HCl, 11·0. $C_{19}H_{23}O_2N,HCl$ requires HCl, 10·9%). This hydrochloride is slightly hygroscopic, dissolves in a small amount of water to give a clear solution which becomes milky on dilution, and is markedly anæsthetic to the tongue.

Diethylaminoethyl Diphenyl-4-carboxylate.—4-Methyldiphenyl (Gomberg and Pernert, *J. Amer. Chem. Soc.*, 1926, **48**, 1375) was converted by oxidation with 2% aqueous permanganate solution (Jacobson, *Ber.*, 1895, **28**, 2547) into the corresponding acid, and this into the acid chloride (m. p. 114°) by thionyl chloride. When the acid chloride (4·6 g.) in benzene was treated with diethylaminoethyl alcohol (2·5 g.), a crystalline deposit was immediately obtained; the reaction was completed by warming the mixture for ½ hour. The product was collected and dissolved in water, impurities were removed by extraction with ether, the base was liberated with dilute sodium carbonate solution and extracted with ether, and the extract was dried with sodium sulphate and treated with hydrogen chloride, the *hydrochloride* of diethylaminoethyl diphenyl-4-carboxylate being precipitated as a white powder, m. p. 183° (Found: HCl, 11·2. $C_{19}H_{23}O_2N,HCl$ requires HCl, 10·9%). This hydrochloride is extremely soluble in water, but the solution becomes milky on dilution.

2′-Cyanodiphenyl-2-carboxylyl Chloride.—Diphenamic acid (16·7 g.) and thionyl chloride were warmed together for ½ hour and the resultant solution was evaporated in a vacuum. A solution of the residual paste in a little benzene was filtered from the needle crystals of diphenimide (1·5 g.), m. p. 217—219°, and diluted with light petroleum, *2′-cyanodiphenyl-2-carboxylyl chloride* being precipitated as a white powder, which crystallised from carbon tetrachloride in stout prisms (10·6 g.), m. p. 84° (Found: C, 69·8; H, 3·2. $C_{14}H_8ONCl$ requires C, 69·6; H, 3·3%). On heating in a vacuum, it gave a pale yellow distillate, b. p. 222°/15 mm., containing about 3% of 4-cyanofluorenone, which remained undissolved by treatment with warm ether and then crystallised from alcohol in long, yellow needles, m. p. 243—244° (Borsche and Sander, *loc. cit.*, give 240°).

Alternatively, the distillate was dissolved in warm sodium hydroxide solution; the 4-cyanofluorenone remained undissolved, and the filtered solution, when poured into dilute hydrochloric acid, gave 2′-cyanodiphenyl-2-carboxylic acid, which crystallised from alcohol in stout needles, m. p. 173° (Werner and Siguet, *Ber.*, 1904, **37**, 4311, give 170—172°).

Diethylaminoethyl 2′-cyanodiphenyl-2-carboxylate was prepared in a similar way to the diphenyl-4-carboxylate. The *hydrochloride* was obtained as white plates, m. p. 189° (Found: HCl, 10·3. $C_{20}H_{22}O_2N_2$,HCl requires HCl, 10·2%), not hygroscopic though moderately easily soluble in water.

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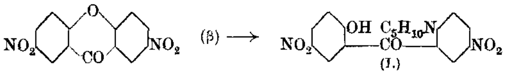
CCCCXXXIII.—*The Interaction of Piperidine with Nitro- and Halogenonitro-derivatives of Xanthone and Diphenylene Oxide.*

By RAYMOND JAMES WOOD LE FÈVRE.

THE interaction of various ethers with piperidine (Le Fèvre, Saunders, and Turner, J., 1927, 1168) suggested a method of comparing the strengths of attachment of radicals to the ethereal oxygen atom. In a similar way attempts have now been made to compare the activities of the ethereal oxygen atoms in diphenyl ether, xanthone, and diphenylene oxide. Owing to the stability of the parent substances the interactions of analogously constituted dinitro-derivatives (the nitro-groups being in each case in the *p*-positions to the ethereal oxygen atom) with piperidine were examined, and the following observations were made.

3 : 6-Dinitrodiphenylene oxide was recovered unchanged after several hours' boiling with piperidine or aniline. α- and β-Dinitroxanthones readily combined with piperidine in the cold, giving unstable yellow substances which, after a few hours' heating at 100°, became yellowish-orange piperidino-compounds (I). The piperi-



(I.)

dino-derivative from α-dinitroxanthone was not obtained in the pure state—a fact explained by the observation that 5 : 5′-*dinitro-2′-piperidino-2-hydroxybenzophenone* (I) lost piperidine at its melting point, the original dinitro-compound being regenerated. The

observations that β-dinitroxanthone could be recovered unchang from boiling aniline, and tetranitroxanthone from boiling piperidi (in both cases coloured addition compounds were formed in tl cold), may similarly be explained by decomposition of the respecti expected products at temperatures lower than the boiling points the reagents.

The interaction of piperidine with 4 : 4′-dinitrodiphenyl ether w fairly rapid and led to normal scission products (Le Fèvre, Saunde and Turner, *loc. cit.*).

Tetrabromodinitroxanthone (Dhar, J., 1916, **109**, 747) react only slowly with piperidine.

In the hope of revealing the orienting influence of oxoniu oxygen the dinitration of 2 : 7-dibromoxanthone was examine The crude dinitration products obtained by the action of nitric ac in acetic acid and in excess of sulphuric acid were boiled wi piperidine. Neither product yielded a perceptible quantity piperidine hydrobromide, but instead 3 : 3′-dibromo-5 : 5′-dinitr 6-piperidino-6′-hydroxybenzophenone was formed. Therefo either oxonium salt formation does not affect nitration in th instance or sulphuric acid solutions of xanthones contain litt quadrivalent oxygen. Since the xanthone structure does n hinder the normal activation of ethereal oxygen by *o*-nitro-grou the possibility that in the above example nitro-groups in tl 3 : 3′-positions could not render bromine atoms in the 2 : 2′-positio labile is small.

EXPERIMENTAL.

Action of Piperidine on α- and β-Dinitroxanthones.—The dinitr xanthones (Dhar, *loc. cit.*) were crystallised from phenol–alcohol.

(1) When α-dinitroxanthone (2 g.) was covered with piperidi (10 c.c.), a bright yellow substance was formed. (If isolated, th lost piperidine and became almost colourless.) The mixture, aft 5 hours' heating on the water-bath, gave a deep red solution, fro which, on dilution with water, an amorphous, yellow powder w obtained which could not be crystallised (Found : N, 10·8—11·1 in different samples).

(2) β-*Dinitroxanthone.* The preliminary development of colo was not so strong as in the preceding case and the yellow compoun dissolved much more slowly. After 10 hours' heating at 100° th mixture was worked up as described above; the 5 : 5′-*dinitr 2′-piperidino-2-hydroxybenzophenone* (I) obtained crystallised fro acetic acid in yellow prisms, m. p. (rapid heating) 155° (Found N, 11·4. $C_{15}H_{17}O_6N_3$ requires N, 11·3%).

When heated slowly, the substance melted at about 150° an changed to a red solid, which became yellower and finally melted a

about 250° to a brown liquid. 4 G. of (I) were therefore heated at 200°. Piperidine was evolved. The brown product was repeatedly extracted with boiling acetic acid and obtained as a cream-coloured powder (Found: N, 9·9. Calc., N, 9·8%), m. p. 260—262° (alone or mixed with β-dinitroxanthone).

5 : 5'-*Dinitro-2'-piperidino-2-acetoxybenzophenone* was prepared by refluxing the piperidino-compound in acetic acid–acetic anhydride, containing anhydrous sodium acetate, until the solution was almost colourless; it was precipitated by water, and crystallised from acetic acid in small needles, m. p. 253—255° (Found: N, 10·8. $C_{20}H_{19}O_7N_3$ requires N, 10·2%).

Action of Aniline on β-Dinitroxanthone.—When 10 g. of β-dinitroxanthone and 35 g. of aniline were mixed in the cold, a red addition compound formed. After 4 hours' boiling, however, β-dinitroxanthone, m. p. 261—262°, was recovered (Found: N, 10·0%). Similar results were obtained with methyl aniline and *o*-toluidine.

Dinitration of 2 : 7-*Dibromoxanthone.*—(*a*) To 1 g. of dibromoxanthone, dissolved in 25 c.c. of concentrated sulphuric acid, 4 c.c. of nitric acid (*d* 1·5) were added; small needles soon began to appear. Cold water was then added and the product was collected, boiled with hot water, and dried on the water-bath; m. p. 208—214° (Found: N, 7·0. Calc. for $C_{13}H_4O_6N_2Br_2$: N, 6·3%). The product reacted readily with piperidine, giving an oily piperidino-compound. The aqueous extracts of the reaction mixture contained no bromine precipitable by silver nitrate. (*b*) A solution of 1 g. of dibromoxanthone in 20 c.c. of nitric acid (*d* 1·5) and 20 c.c. of glacial acetic acid was warmed at 90° for 6 hours. The product, on treatment with piperidine, gave the same result as before, the absence of nitro-groups in any of the 1 : 3 : 6 : 8-positions being thus indicated.

2 : 7-*Dibromo*-4 : 6-*dinitroxanthone* was prepared by allowing 3 g. of dibromoxanthone to dissolve in 60 c.c. of fuming nitric acid at about 60°. The product was isolated in the usual way; after being extracted with a little benzene and crystallised from much benzene, it had m. p. 265—266° (Found: N, 6·4. $C_{13}H_4O_6N_2Br_2$ requires N, 6·3%). The action of piperidine on it gave a gummy product which could not be separated.

Nitration of β-Dinitroxanthone.—A solution of 10 g. of the dinitro-compound in 100 c.c. of sulphuric acid and 100 c.c. of fuming nitric acid was heated on a water-bath for 3 hours. Dilution with water then gave 2 : 4 : 5 : 7-*tetranitroxanthone* as a white powder, not molten at 300° (Found: N, 14·8. $C_{13}H_4O_{10}N_4$ requires N, 14·9%).

Action of Piperidine on 2 : 4 : 5 : 7-*Tetranitroxanthone.*—When the reactants were mixed in the cold a bright red colour developed, but

after the mixture had been heated for 8 hours at 100°, the tetranitro-compound was recovered (Found: N, 15·0%).

Piperidine reacted vigorously with 6-nitropiperonal, giving a tar from which no individual was isolated.

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CCCCXXXIV.—*Researches on Residual Affinity and Co-ordination. Part XXXI. Molybdyl Bis-β-diketones.*

By GILBERT T. MORGAN and REGINALD ARTHUR SALTER CASTELL.

CHEMICAL literature contains references to two molybdenum derivatives of acetylacetone (Beilstein, 1918, Vol. I, p. 783): molybdous acetylacetone, formulated as $Mo(C_5H_7O_2)_2$ by Gach (*Monatsh.*, 1900, **21**, 112), and molybdyl bisacetylacetone, $MoO_2(C_5H_7O_2)_2$, first prepared by Rosenheim and Bertheim (*Z. anorg. Chem.*, 1903, **34**, 439). The composition indicated by Gach for his compound is extremely improbable, as his method of production is very similar to that employed by Rosenheim and Bertheim and in both experiments the starting material is some form of molybdenum trioxide. These two preparations have now been repeated and both products have been completely analysed and found to be identical.

In spite of the reducing action of acetylacetone on molybdenum trioxide and its hydrates, this reduction is subsidiary to the condensation occurring between unreduced trioxide and the diketone.

We have not been able to confirm the existence of molybdous acetylacetone, Gach's compound being undoubtedly molybdyl bisacetylacetone. The condensation has been shown to be a general reaction by the preparation of other molybdyl bis-β-diketones. Interaction occurs between molybdenum trioxide and such aliphatic diketones as propionylacetone, dipropionylmethane, and 3-ethylacetylacetone, and also with benzoylacetone and dibenzoylmethane containing aromatic radicals. Determinations of valency by Wardlaw's method (J., 1923, **123**, 969) show in all cases the presence of sexavalent molybdenum.

The discovery of a new hydrated molybdenyl monochloride by

Wardlaw and Wormell (J., 1924, **125**, 2370) afforded an opportunity of obtaining an acetylacetone derivative containing molybdenum in a lower state of oxidation, and by this means a hydrated *molybdenyl acetylacetone*, $MoO(C_5H_7O_2),2\frac{1}{2}H_2O$, has been realised.

Experiments made with molybdenum pentachloride and molybdenum oxysulphate, $Mo_2O_3(SO_4)_2$, showed that the tendency for quinquevalent molybdenum to yield acetylacetone derivatives is comparatively slight, although a green compound having the composition $MoO_2(C_5H_7O_2)$ was obtained by the aërial oxidation of molybdenyl acetylacetone.

EXPERIMENTAL.

Molybdyl Bisacetylacetone, $MoO_2(Me{\cdot}CO{\cdot}CH{\cdot}COMe)_2$.—On analysing the yellow substance prepared by the interaction of molybdenum trioxide and acetylacetone, Gach obtained Mo, 32·90%, corresponding with $Mo(C_5H_7O_2)_2$, which requires Mo, 32·65%; the proportions of carbon and hydrogen were not determined by him. The preparation was repeated by leaving molybdenum trioxide and acetylacetone in a closed vessel for 4 days; yellow crystals had then appeared among the trioxide, which meanwhile had undergone slight reduction to the oxide. These crystals were dissolved out by alcohol and crystallised repeatedly from this solvent. The compound, *which was also soluble in chloroform, benzene, toluene, or* acetone to yellow solutions, was insoluble in water, ether, or light petroleum; it melted at 175° and decomposed above 230° (Found: C, 36·8; H, 4·0; Mo, 29·1. Calc. for $C_{10}H_{14}O_6Mo$: C, 36·8; H, 4·3; Mo, 29·5%). A valency determination by Wardlaw's method showed that the molybdenum present was sexavalent and not bivalent.

The preparation was modified by heating together under reflux, in a stream of carbon dioxide, 7 g. of molybdenum trioxide, 10 g. of acetylacetone, and 20 c.c. of alcohol. The trioxide gradually became blue by reduction and the liquid assumed a dark green colour. On cooling, golden-yellow crystals separated which were picked out from co-precipitated blue oxide and recrystallised from alcohol. The green mother-liquor yielded further crops of crystals (Found: Mo, 29·3%).

Rosenheim and Bertheim (*loc. cit.*) condensed acetylacetone in alcoholic solution with either powdered molybdic oxide dihydrate, dimethyl molybdate, or oxalomolybdic acid; on boiling for a short time, yellow microscopic crystals separated. Complete analysis of this preparation gave data corresponding with $MoO_2(C_5H_7O_2)_2$.

For comparison with the compound described by Gach we prepared molybdic trioxide dihydrate by adding successively to a 15%

solution of ammonium molybdate, 30% nitric acid, and ammonium nitrate until the solution contained 10% of this salt. After 8 days a small amount of dihydrate had separated, and precipitation was hastened by scratching the sides of the containing vessel (Found: Mo, 53·2. Calc. for $MoO_3,2H_2O$: Mo, 53·3%). Six grams of this dihydrate were heated for 4 hours with 7 g. of acetylacetone in alcoholic solution. The solution, filtered from blue oxide, yielded canary-yellow crystals insoluble in water but soluble in acetone, acetylacetone, benzene, or chloroform. From these media the product crystallised in six-sided plates melting at 175° and decomposing above 230° (Found: C, 36·7; H, 4·0; Mo, 29·5%). A mixed melting-point determination with the preparation from Gach's experiment showed that the two products were identical. In both experiments a portion of the trioxide was reduced to blue oxide, which, when suspended or dissolved colloidally in the yellow alcoholic solution, rendered this liquid green. If the product is crystallised from this solution, it may become contaminated with blue Mo_3O_8, only 8% of which would be required to give a molybdenum content of 32·90% corresponding with Gach's determination of the metal. Moreover, this impurity in the molybdyl bisacetylacetone induces thermal decomposition at a temperature much lower than the melting point of the pure substance.

Molybdyl Bispropionylacetone, $MoO_2(Et{\cdot}CO{\cdot}CH{\cdot}COMe)_2$.—When molybdenum trioxide (1·4 g.) and 2·2 g. of propionylacetone were heated together on the water-bath, a viscid mass resulted which was washed with ether and dissolved in chloroform; the product was precipitated from this solution by addition of light petroleum. When crystallised from alcohol, the substance separated in small, brown, rhombic crystals melting at 185°, whereas from hot chloroform more fusible green crystals separated (m. p. 130°). The *compound* was soluble in alcohol, chloroform, benzene, or acetone, but insoluble in water, ether, or light petroleum (Found: C, 40·5; H, 5·3; Mo, 27·0. $C_{12}H_{18}O_6Mo$ requires C, 40·7; H, 5·1; Mo, 27·2%).

Molybdyl Bisdipropionylmethane, $MoO_2(Et{\cdot}CO{\cdot}CH{\cdot}COEt)_2$.—A mixture of 1·4 g. of molybdenum trioxide and 2·5 g. of dipropionylmethane was heated until the trioxide had disappeared. The brown, viscid mass was washed with ether and extracted with alcohol. The alcoholic solution gave brown, six-sided plates, m. p. 78°, which were soluble in alcohol, acetone, chloroform, benzene, or toluene (Found: C, 44·25; H, 5·9; Mo, 25·4. $C_{14}H_{22}O_6Mo$ requires C, 44·0; H, 5·8; Mo, 25·1%).

Molybdyl Bis-3-ethylacetylacetone, $MoO_2(Me{\cdot}CO{\cdot}CEt{\cdot}COMe)_2$.—On heating together molybdenum trioxide and 3-ethylacetylacetone,

the mixture became brown and set to a viscid mass. Extraction as in previous examples removed a brown, crystalline solid, soluble in alcohol, acetone, chloroform, or benzene (Found: C, 43·3; H, 5·1; Mo, 25·8. $C_{14}H_{22}O_6Mo$ requires C, 44·0; H, 5·8; Mo, 25·1%).

Molybdyl Bisbenzoylacetone, $MoO_2(Ph{\cdot}CO{\cdot}CH{\cdot}COMe)_2$.—A mixture of 1·5 g. of molybdenum trioxide and 3·25 g. of benzoylacetone was warmed on the water-bath until the oxide had disappeared; the melt was then allowed to cool to a viscid mass. This, after being washed with ether, was extracted with alcohol; the extract yielded brown, rhombic crystals, m. p. 98°, soluble in acetone, chloroform, benzene, or toluene, but insoluble in water, ether, or light petroleum (Found: C, 53·8; H, 4·1; Mo, 21·3. $C_{20}H_{18}O_6Mo$ requires C, 53·3; H, 4·0; Mo, 21·3%).

Molybdyl Bisdibenzoylmethane, $MoO_2(Ph{\cdot}CO{\cdot}CH{\cdot}COPh)_2$.—On heating together 1·5 g. of molybdenum trioxide and 4·5 g. of dibenzoylmethane, a dark brown solid resulted which was washed successively with ether and alcohol, and the residue extracted with chloroform. From the cold extract a substance separated in light brown needles, m. p. 112°, soluble in alcohol, acetone, benzene, and toluene, but not in water, ether, or light petroleum (Found: C, 62·1; H, 4·3; Mo, 16·6. $C_{30}H_{22}O_6Mo$ requires C, 62·7; H, 3·8; Mo, 16·7%).

Molybdenyl Acetylacetone, $MoO(Me{\cdot}CO{\cdot}CH{\cdot}COMe),2\frac{1}{2}H_2O$.—By heating together for several hours 1·5 g. of molybdenyl chloride, $MoOCl,4H_2O$ (Wardlaw and Wormell, *loc. cit.*), and 1 g. of acetylacetone in alcoholic solution, a deep red liquid was obtained which on evaporation furnished brown, cubical crystals of hydrated *molybdenyl acetylacetone*. This product was recrystallised from alcohol and dried out of contact with air. It was soluble in water, but insoluble in anhydrous organic media. The dark red solution in alcohol or water was decolorised by dilute acids or alkalis; warm potassium ferrocyanide developed a yellowish-green fluorescence which changed to greenish-blue on cooling. The aqueous solution reduced cold silver nitrate and a valency determination indicated tervalent molybdenum. The compound decomposed indefinitely at about 150° (Found: C, 23·6; H, 4·2; Mo, 37·2; H_2O, 17·7. $C_5H_7O_3Mo,2\frac{1}{2}H_2O$ requires C, 23·4; H, 4·7; Mo, 37·5; H_2O, 17·6%). The water was estimated by heating the compound at 120° in a stream of nitrogen, the water evolved being collected in sulphuric acid.

In an endeavour to estimate the water by difference the compound was heated in the air at 120°; oxidation occurred slowly and a green residue was left. This substance, which was hygroscopic in

air, decomposed at 150° and dissolved to a green solution in water, alcohol, chloroform, or benzene (Found: C, 26·3; H, 3·8; Mo, 42·7. $C_5H_7O_4Mo$ requires C, 26·4; H, 3·1; Mo, 42·3%). Accordingly these data correspond with a derivative of quinquevalent molybdenum.

The authors desire to thank the Birmingham University Research Committee for a grant which has helped to defray the cost of this investigation.

University of Birmingham,
Edgbaston. [*Received, November* 3*rd*, 1928.]

CCCCXXXV.—*The Inhibition of Chemical Reactions. Part II. The Mechanism of the Inhibition of Esterification by Alkaline Substances.*

By Kenneth Claude Bailey.

The author has recently demonstrated (this vol., p. 1204) that the reaction of ethyl alcohol and acetic acid takes place in two ways, (*a*) in the body of the liquid, and (*b*) on the surface of the containing glass vessel, and that the reaction of type (*b*) is inhibited by the presence of a trace of pyridine (one part or less per 10,000 parts), whilst the reaction of type (*a*) is only slightly affected, even by the addition of much larger quantities of pyridine.

The following mechanism is suggested. The surface of the vessel contains a number of active areas, at which pyridine molecules are adsorbed. Molecules of alcohol and acid, possessing sufficient energy to react, come into contact on an active area, forming a complex. In the absence of an inhibitor, this complex undergoes re-arrangement and breaks up into water and ethyl acetate. If a molecule of pyridine is present on the glass surface immediately beside the alcohol–acid complex, it attracts the acetic acid, withdraws it from the complex, and returns with it into the solution as pyridine acetate which dissociates, regenerating pyridine and acetic acid.

If we assume that a considerable proportion of the added pyridine is adsorbed on the surface, alcohol–acid complexes which form in the body of the liquid, with sufficient energy to react, are unlikely to meet a pyridine molecule when this base is present in small concentration, and reaction of type (*a*) is therefore scarcely affected.

This hypothesis, according to which the function of pyridine as an inhibitor depends on its nature as a weak base, has been tested by

experiments on the effect of quinoline, piperidine, ammonia, sodium hydroxide, benzyl chloride, *m*-cresol, benzene, chloroform, and hydrogen chloride on the reaction of ethyl alcohol and acetic acid.

Hydrogen chloride acted, of course, as a powerful positive catalyst, and was included as a control. Benzyl chloride, *m*-cresol, benzene, and chloroform either encouraged the reaction slightly or had no pronounced effect. Quinoline, piperidine, ammonia, and sodium hydroxide gave curves of exactly the same type as pyridine. The inhibiting action became more marked with increase of basic strength in passing from quinoline to pyridine and thence to piperidine, which almost completely inhibited reaction of type (*b*) in a concentration of about 1 in 30,000. The action of ammonia was rather less marked, and that of sodium hydroxide still less marked. This was no doubt due to the fact that these inorganic bases existed in solution as acetates to a greater extent than the organic bases.

The present interpretation, if correct, indicates that sodium and ammonium acetates, present in low concentration in alcoholic acetic acid solution, are highly dissociated on the glass surface, the basic constituent being adsorbed. Dissociation by adsorption has been observed by Bartell and Miller (*J. Amer. Chem. Soc.*, 1923, **45**, 1106), Miller (*ibid.*, 1924, **46**, 1150) and others.

EXPERIMENTAL.

The reaction mixture, which consisted of 9·275 mols. of ethyl alcohol per mol. of acetic acid, was placed in a specific gravity bottle of 25 c.c. capacity, closed by a ground-glass stopper with capillary aperture. This was completely filled and inverted in a wide test-tube containing solution of the same composition. The test-tube was closed by a loosely-fitting cork stopper and placed in an incubator at 43°. Five bottles of similar type were used, and as it had been shown by preliminary experiments that they gave almost identical esterification velocities, it was assumed that they possessed surfaces of equal activity.

Four or five mixtures, of which one was a control and the others contained varying amounts of inhibitor, were placed in the incubator simultaneously, so that slight variations of temperature affected equally all solutions of a series. At the close of an experiment the solutions were removed simultaneously, poured into cold water, and analysed as rapidly as possible.

In the table, esterification during 20 hours at 43° in absence of a catalyst is taken as standard (100), and other results are expressed in terms of this.

Conc. of added substance (mols. per 100,000 mols. of reaction mixture)	Nil.	3·34	8·34	83·4
		Esterification.		
Added substance.				
Quinoline	*100*	*68·5*	*50·5*	22·8
Pyridine	100	57·0	38·8	20·4
Piperidine	100	25·0	19·0	14·0
Ammonia	100	28·8	23·3	20·0
Sodium hydroxide	100	43·1	27·0	20·2
Hydrogen chloride	100	199	326	749
Benzyl chloride	100	107·9	115	137·5
m-Cresol	100	97·4	104·1	114·2
Benzene	100	101·5	102·3	105·4
Chloroform	*100*	*92·4*	*99·6*	111·5

TRINITY COLLEGE, DUBLIN. [*Received, September 13th*, 1928.]

CCCCXXXVI.—*The Rotation Dispersion and Circular Dichroïsm of Caryophyllene Nitrosite.*

By STOTHERD MITCHELL.

Rotation Dispersion.—Deussen (*Annalen*, 1912, **388**, 161) found that caryophyllene nitrosite in benzene had $[\alpha]_D + 1626°$, and later (*J. pr. Chem.*, 1912, **85**, 487) he showed that this remarkably high value varies considerably with concentration and is always greater for sodium light than for mercury green. The latter observation and the blue colour of the substance led Tschugaev to suggest (*ibid.*, **86**, 547) that it might show the Cotton effect,* *i.e.*, a maximum of rotation on one side of its absorption band and a minimum on the other. To settle this point the author has examined the rotation dispersion of a solution of caryophyllene nitrosite in alcohol. The results obtained are shown in Fig. 1. The rotation reaches a maximum positive value about 6250 Å.U., becomes zero at 6800 Å.U., and is thereafter negative. Subsequent examination of the absorption spectra has revealed a narrow band with its head about 6800 Å.U., thereby confirming Tschugaev's contention.

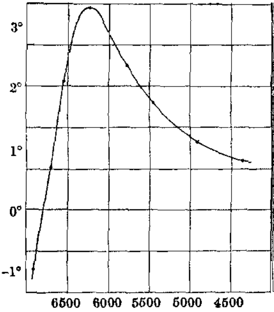
The caryophyllene nitrosite was prepared essentially as described by Schreiner and Kremers (*Pharm. Arch.*, 1899, **2**, 282); after crystallisation first from alcohol and then from aqueous acetone it melted at 115°. The alcoholic solution for rotation measurements contained 0·3113 g. of caryophyllene nitrosite per 100 g. of solution, and was contained in a 6-cm. tube. The readings were taken at 20° and the solution had $d_{4°}^{20°}$ 0·7932. Eight different colours of light were used. A mercury-vapour lamp supplied the yellow, green,

* This phenomenon was first observed by Cotton (*Ann. Chim. Phys.*, 1896, **8**, 347) with alkaline solutions of copper tartrate and with potassium chromium tartrate.

and violet ones direct, and narrow strips of the spectrum from a Nernst lamp, corresponding to four other fainter mercury lines and to the red hydrogen line, were utilised in the manner described by Patterson (J., 1916, **109**, 1143). Readings were not continued beyond 6908 Å.U.; indeed, some difficulty was experienced in taking this. The values obtained were :

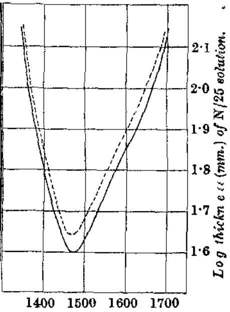
λ	4358	4916	5461	5790	6234	6563	6717	6908
a	0·78°	1·07°	1·71°	2·31°	3·27°	2·06°	0·66°	−0·97°
$[a]$	526°	722°	1154°	1559°	2207°	1390°	459°	−655°

FIG. 1.



λ, in Å.U.

FIG. 2.



Oscillation frequencies.

——— *Left-handed circularly polarised light.*
- - - - - *Right-handed ,, ,, ,,*

Circular Dichroïsm.—It has been shown by Fresnel that when a beam of plane-polarised light enters a transparent optically active medium it is resolved into two circularly polarised beams (one right-handed and the other left-handed). These travel with different velocities through the medium and combine again on leaving it to give a plane-polarised beam, the plane of polarisation of which is rotated through a certain angle from that of the original beam. Cotton found that in the region of selective absorption the emergent light from his coloured tartrate solutions was elliptically polarised, and he explained this by supposing that, besides travelling at different speeds, the circularly polarised components were absorbed to different extents. This view was subsequently confirmed by direct experiments with right- and left-handed circularly polarised monochromatic light, and by analogy with the dichroïsm of doubly refracting crystals the phenomenon was called circular dichroïsm.

Cotton's work on this subject has been extended to other metallic complexes of tartaric acid and to similar compounds of malic and lactic acids by McDowell (*Physical Rev.*, 1905, **20**, 163), Olmstead (*ibid.*, 1912, **35**, 31), and by Bruhat (*Ann. Physique*, 1915, **3**, 232; 1920, **13**, 36). The last author has also studied the phenomenon with the diphenyldithiourethanes of *d*- and *l*-borneol (*loc. cit.*) and with potassium irido-oxalate (*Bull. Soc. chim.*, 1915, **17**, 223). These, however, appear to be the only cases hitherto recorded, and it is therefore of interest to find a further example in caryophyllene nitrosite.

The above authors have concerned themselves more particularly with the variation of ellipticity (*i.e.*, the ratio of the axes of the elliptical light) with wave-length, but in the present investigation the absorption spectra for right- and left-handed light in the region of selective absorption have been studied. A Fresnel quartz tri-prism (*Ann. Chim. Phys.*, 1825, **28**, 147) was used to produce accurately both right- and left-handed circularly polarised light of equal intensity and contiguous to each other. The centre prism had a refracting angle of 150° and the base was 4″ long. The tri-prism was inserted between the collimator and the prism of a Hilger constant-deviation spectroscope, the collimator being displaced the necessary distance from its usual position. A 500-c.p. Pointolite lamp was employed as source of light. The height of the slit was adjusted with a **V**-shaped metal slide until the two spectra, produced one above the other by the tri-prism, just ceased to overlap. The Baly tube containing the caryophyllene nitrosite solution (*N*/25 in alcohol) was placed between the light source and the spectroscope slit. The eye-piece of the telescope was then removed and replaced by a single lens and camera, and a series of photographs was taken on a panchromatic plate for different thicknesses of solution. For calibration purposes the Baly tube was removed and a cobalt arc was photographed at the top and at the bottom of the plate. The results are represented graphically in Fig. 2. A distinct difference between the absorption spectra for right- and for left-handed circularly polarised light is apparent.

UNIVERSITY OF GLASGOW. [*Received, November 8th,* 1928.]

CCCCXXXVII.—*Interactions of Selenium Oxychloride and Phenols.*

By GILBERT T. MORGAN and FRANCIS HEREWARD BURSTALL.

IN two communications on organic selenium compounds formerly published from the Rostock Laboratories, Michaelis and Kunckell described certain reactions between selenium oxychloride or tetra-

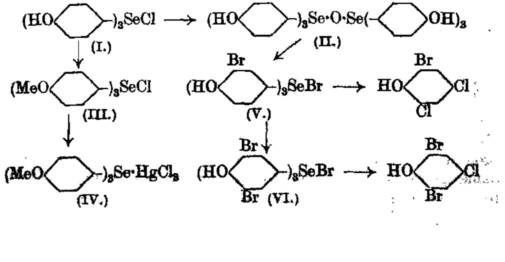
chloride and the phenols and phenolic ethers (*Ber.*, 1895, **28**, 609; 1897, **30**, 2823). The second of these publications contains a short description of condensations effected in ethereal solution between selenium oxychloride and phenol, β-naphthol and resorcinol, wherein the two monohydric phenols are stated to give selenides of the type $Se(R{\cdot}OH)_2$, R being C_6H_4 or $C_{10}H_6$, whilst resorcinol is alleged to yield a selenyl derivative, $SeO[C_6H_3(OH)_2]_2$.

On repeating the condensations we have been able to confirm these statements only in the case of β-naphthol, which gives the selenide, $Se(C_{10}H_6{\cdot}OH)_2$, in ethereal or preferably in chloroform solution.

The interactions of selenium oxychloride with phenol, the cresols, resorcinol, β-naphthol, and salicylic acid have now been investigated with the following results:

1. *Phenol.* When condensed with selenium oxychloride either in ethereal or in chloroform solution, phenol yields two isomeric *selenonium chlorides*, $[(HO{\cdot}C_6H_4)_3Se]Cl$, each containing ionisable chlorine precipitable as silver chloride and replaceable by other acidic radicals. The complex kation of these selenonium chlorides includes three phenolic hydroxyl groups which confer acidic properties on the chlorides so that these salts dissolve in aqueous caustic alkalis. From such solutions carbonic or acetic acid precipitates the amphoteric *oxide*, $[(HO{\cdot}C_6H_4)_3Se]_2O$, which redissolves in alkalis and reacts with acids to furnish the corresponding *bromide*, *nitrate*, *sulphate* and *chloroplatinate*.

The less soluble of the two selenonium chlorides, which is the main condensation product, is proved to be *tri-4-hydroxytriphenylselenonium chloride* (I) by progressive halogenation, for when neutralised with acetic acid, an alkaline solution of selenonium chloride deposits the *oxide* (II), which on bromination yields successively a tribrominated bromide (V) and a hexabrominated bromide (VI). With chlorine water the former of these bromides gives 2 : 4-dichloro-6-bromophenol, whereas the latter furnishes 4-chloro-2 : 6-dibromophenol.

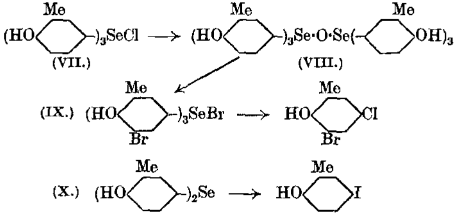


With the orientation of selenium and hydroxyl radicals established in these compounds it becomes possible to determine the constitution of trianisylselenonium chloride formerly prepared by Hilditch and Smiles (J., 1908, **93**, 1384), who, on employing a modified Friedel–Crafts reaction, obtained only selenonium salts from anisole, phenetole and resorcinol dimethyl ether.

Tri-4-hydroxytriphenylselenonium chloride is methylated to the oily *tri-4-methoxytriphenylselenonium chloride* (III), which is converted into crystalline *mercurichloride* (IV). This complex salt is compared with a specimen prepared from trianisylselenonium chloride obtained by the method of Hilditch and Smiles. Both mercurichlorides melt as one compound at 68—70°.

Owing to the comparatively small yield of the more soluble selenonium chloride, the constitution of this salt was not determined; it is evident, however, that one, two, or three of its hydroxyl groups must be in the ortho-position with respect to selenium.

2. o-*Cresol.* The main product of the selenium oxychloride condensation is *tri-4-hydroxytri-3-methyltriphenylselenonium chloride* (VII), the constitution of which is ascertained by progressive halogenation, starting with the corresponding *oxide* (VIII), which

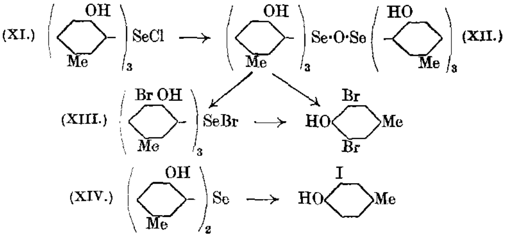


yields a tribrominated bromide (IX) decomposed by chlorine water to furnish 5-chloro-3-bromo-*o*-cresol.

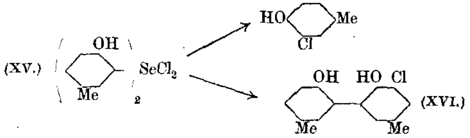
Di-4-hydroxydi-3-methyldiphenyl selenide (X), which arises as a by-product in the condensation of *o*-cresol and selenium oxychloride, is decomposed on boiling with hydriodic acid to yield 5-iodo-*o*-cresol.

3. p-*Cresol.* A similar halogenation suffices to characterise *tri-2-hydroxytri-5-methyltriphenylselenonium chloride* (XI), a product of the selenium oxychloride condensation with *p*-cresol. Its *oxide* (XII) furnishes a tribrominated bromide (XIII) with anhydrous bromine, whereas with bromine water this bromide or the original oxide gives rise to 3 : 5-dibromo-*p*-cresol. In addition to the foregoing selenonium chloride, *p*-cresol yields a considerable pro-

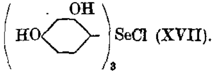
portion of *di-2-hydroxydi-5-methyldiphenyl selenide* (XIV), which on treatment with hydriodic acid gives 3-iodo-*p*-cresol.



The phenols have not in the condensations under review yielded chlorinated selenium derivatives of the type $Cl_2Se(R{\cdot}OH)_2$, although analogous compounds, $Cl_2Se(R{\cdot}OX)_2$, with $X = CH_3$ or C_2H_5, were obtained by Kunckell (*loc. cit.*) from anisole and phenetole. The absence of such chlorinated derivatives in the phenolic condensations is probably due to the readiness with which the phenols undergo chlorination. The mother-liquors from the selenide (XIV) contain 3-chloro-*p*-cresol and also a chlorinated dicresol (XVI). These substances may arise from the autochlorination of the hypothetical dichloroselenide (XV).



4. ***Resorcinol.*** In its condensation with selenium oxychloride resorcinol resembles phenol in giving rise to a selenonium chloride having the constitution



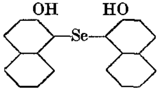
(XVII).

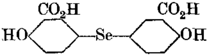
5. β-***Naphthol.*** This condensation proceeds quantitatively in the sense of the equation

$$3C_{10}H_7{\cdot}OH + SeOCl_2 = Se(C_{10}H_6{\cdot}OH)_2 + C_{10}H_6Cl{\cdot}OH + HCl + H_2O.$$

Di-2-hydroxydi-1-naphthyl selenide (XVIII) is decomposed by

warm hydriodic acid into 1-iodo-β-naphthol and selenium, and a similar attack by bromine furnishes 1-bromo-β-naphthol.

(XVIII.) 


(XIX.)

6. *Salicylic acid.* The condensation, effected preferably in the absence of solvent, leads to a disalicylyl selenide (*di-4-hydroxydiphenyl selenide di-3-carboxylic acid*, XIX).

The foregoing results indicate that between selenium oxychloride and the phenols two modes of reaction may take place, one manifested by phenol and resorcinol :

1. $3H\cdot R\cdot OH + SeOCl_2 = (HO\cdot R)_3SeCl + HCl + H_2O$,

and another exemplified by β-naphthol and salicylic acid :

2. $3H\cdot R\cdot OH + SeOCl_2 = Se(R\cdot OH)_2 + Cl\cdot R\cdot OH + HCl + H_2O$.

With *o*- and *p*-cresols both interactions occur concurrently.

EXPERIMENTAL.

1. *Phenol and Selenium Oxychloride.*—On adding selenium oxychloride (33·2 g. ; 1 mol.), diluted with 50 c.c. of chloroform, to a well-stirred solution of phenol (56·4 g. ; 3 mols.) in 500 c.c. of the same solvent, the mixture darkened rapidly and became opaque owing to separation of insoluble matter; meanwhile heat was generated and hydrogen chloride evolved. After an hour the yellow solution containing in suspension a deep red oil was refluxed until the insoluble product adhered to the containing vessel as a semi-solid, yellow gum. The chloroform was decanted and the residue triturated with acetone; the selenonium chloride then separated as a white powder which crystallised from alcohol–ether in small, white prisms, m. p. 232° (decomp.) (Found : C, 53·9; H, 4·0; Se, 19·8, 20·4; Cl, 9·2. $C_{18}H_{15}O_3ClSe$ requires C, 54·85; H, 3·8; Se, 20·1; Cl, 9·0%).

Tri-4-hydroxytriphenylselenonium chloride (I), a stable salt, dissolved readily in hot water to an almost neutral solution (p_H 5·7); it separated on cooling from hot water or alcohol in an anhydrous condition as a microcrystalline powder. It was insoluble in the other organic media. Cold, concentrated sulphuric acid dissolved it to a colourless solution with evolution of hydrogen chloride; on warming, yellow to green tints were developed. Aqueous ferric chloride gave a reddish-purple coloration, and aqueous caustic soda dissolved the selenonium chloride to a pale yellow solution from

which carbon dioxide or the calculated amount of dilute acetic acid precipitated white, amorphous *tri-4-hydroxytriphenylselenonium oxide* (II), decomp. 240° (Found: C, 58·2; H, 4·2; Se, 21·9, 21·7. $C_{36}H_{30}O_7Se_2$ requires C, 59·0; H, 4·1; Se, 21·6%).

This complex amphoteric oxide was insoluble in neutral organic media but furnished salts with mineral acids. The sulphate and bromide, decomposing respectively at 269—270° and 237°, are prepared by adding the appropriate acid to alkaline solutions of the oxide. The bromide crystallised from alcohol–ether in white needles. With an alcoholic solution of the selenonium chloride, silver nitrate gave a quantitative deposition of silver chloride; the filtrate on evaporation and addition of ether yielded the white, crystalline, water-soluble *nitrate*, m. p. 138—139° (decomp.) (Found: N, 3·4. $C_{18}H_{15}O_6NSe$ requires N, 3·3%).

From a hot aqueous solution of selenonium and platinic chlorides an orange *chloroplatinate* crystallised, on cooling, in lustrous needles, decomp. 244° (Found: Pt, 17·4. $C_{36}H_{30}O_6Cl_6Se_2Pt$ requires Pt, 17·4%).

Tri-4-methoxytriphenylselenonium chloride (III). Five g. of methyl iodide were added to a solution of tri-4-hydroxytriphenylselenonium chloride (3·9 g.) and sodium methoxide (1 g. of sodium in 200 c.c. of methyl alcohol), the mixture being refluxed until acid to litmus. After being acidified strongly with hydrochloric acid, the mixture was distilled in steam, and the residue was dissolved in chloroform, dried, and evaporated to a yellow, uncrystallisable gum which, however, yielded *tri-4-methoxytriphenylselenonium mercurichloride* (IV), m. p. 68—70°, identical with the mercurichloride obtained from trianisylselenonium chloride prepared by the method of Hilditch and Smiles (*loc. cit.*) (Found: Cl, 14·4. $C_{21}H_{21}O_3Cl_3SeHg$ requires Cl, 15·05%).

Tri-3-bromotri-4-hydroxytriphenylselenonium bromide (V). Tri-4-hydroxytriphenylselenonium oxide was stirred gradually into excess of bromine and when the vigorous reaction had subsided the mixture was evaporated to dryness; the dry residue after trituration with ether left a white, brominated product which was dissolved in hot alcohol. This solution deposited a crop of impure hexabrominated bromide (*v. infra.*); the mother-liquor on evaporation and addition of ether yielded the tribrominated bromide as a white, microcrystalline powder. After repeated crystallisation this *bromide* melted at 251° to a red liquid (Found: Br, 47·4; Se, 11·4. $C_{18}H_{12}O_3Br_4Se$ requires Br, 47·4; Se, 11·7%). The tribrominated bromide was insoluble in water and organic media except alcohol, but dissolved readily in aqueous caustic soda; dilute acetic acid precipitated the complex oxide (m. p. 198°), which was decomposed

readily by chlorine water, yielding 2 : 4-dichloro-6-bromophenol, m. p. 67—68°.

Tri-3 : 5-*dibromotri*-4-*hydroxytriphenylselenonium bromide* (VI) was precipitated in the more sparingly soluble fraction from the foregoing experiment in combination with the tribrominated bromide. Repeated evaporation with bromine and crystallisation from alcohol led to the pure hexabrominated *bromide*, obtained in sparingly soluble, lustrous, white prisms, decomp. 261° (Found : Br, 61·6. $C_{18}H_9O_3Br_7Se$ requires Br, 61·35%). Chlorine water eliminated selenium from this hexabrominated salt and furnished 4-chloro-2 : 6-dibromophenol, m. p. 92°.

Isomeric trihydroxytriphenylselenonium chloride,

$(HO{\cdot}C_6H_4)_3SeCl,2H_2O$.

The acetone filtrates from tri-4-hydroxytriphenylselenonium chloride yielded on evaporation an isomeric *selenonium chloride*, crystallising with two molecular proportions of water and decomposing at 125° (Found : C, 50·6 ; H, 4·5 ; Se, 18·6 ; Cl, 8·0 ; loss on heating at 110°, 9·5. $C_{18}H_{15}O_3ClSe,2H_2O$ requires C, 50·3 ; H, 4·45 ; Se, 18·4 ; Cl, 8·4 ; loss, 8·4%). This salt dissolved in hot water, but separated on evaporation as a colourless, viscous gum setting to a glass over sulphuric acid. It possessed the chemical properties of the tri-*p*-isomeride, but the small yield (1—2 g.) rendered orientation experiments impracticable. From a solution in aqueous caustic soda, carbon dioxide or dilute acetic acid precipitated the amorphous oxide (decomp. 180°), and methylation yielded successively a viscid trimethoxytriphenylselenonium chloride and a mercurichloride (m. p. 54—55°).

2. o-*Cresol and Selenium Oxychloride*.—Selenium oxychloride (16·6 g. ; 1 mol.) in 50 c.c. of chloroform was stirred into a solution of *o*-cresol (38·6 g. ; 3 mols.) in 400 c.c. of the same solvent. After an hour the mixture was refluxed until the heavy, red oil which first separated became converted into solid selenonium salt. The chloroform solution was decanted; the residue, after being washed with acetone, crystallised from alcohol–ether as a white powder, decomp. 231° (yield, 10 g.) (Found : C, 57·7 ; H, 5·1 ; Cl, 7·9 ; Se, 17·8. $C_{21}H_{21}O_3ClSe$ requires C, 57·8 ; H, 4·9 ; Cl, 8·1 ; Se, 18·2%).

Tri-4-*hydroxytri*-3-*methyltriphenylselenonium chloride* (VII) was insoluble in water and most organic solvents but dissolved in alcohol. Alcoholic ferric chloride gave no coloration, but warm concentrated sulphuric acid produced a green tint. When an alkaline solution of this chloride was treated with carbon dioxide or dilute acetic acid the corresponding *selenonium oxide* (VIII) was precipitated as an amorphous powder, decomp. 236° (Found : Se, 19·6. $C_{42}H_{42}O_7Se_2$ requires Se, 19·4%).

The addition of nitric acid to an alkaline solution of this oxide gave the *nitrate*, decomp. 224°, which was crystallised from alcohol (Found : N, 3·3. $C_{21}H_{21}O_6NSe$ requires N, 3·0%).

Tri-5-bromotri-4-hydroxytri-3-methyltriphenylselenonium bromide (IX) was produced on stirring small quantities of the foregoing oxide into excess of bromine. Hydrogen bromide was evolved and after the violent reaction had subsided the mixture was taken to dryness; after being triturated with ether, the white residue was crystallised from boiling alcohol, the brominated *bromide* separating in silvery prisms darkening and decomposing at 253° (Found: Br, 44·8. $C_{21}H_{18}O_3Br_4Se$ requires Br, 44·6%). When added to an alkaline solution of this brominated selenonium bromide, dilute acetic acid precipitated the amorphous oxide, which was decomposed by chlorine water, giving 5-chloro-3-bromo-*o*-cresol (m. p. 48°).

Di-4-hydroxydi-3-methyldiphenyl selenide (X). After tri-4-hydroxytri-3-methyltriphenylselenonium chloride had been separated in the selenium oxychloride condensation, the chloroform filtrate was evaporated to a viscid oil and distilled in steam. A little unchanged *o*-cresol appeared first, but the main distillate consisted of 5-chloro-*o*-cresol (m. p. 48°). The brown, gummy residue was extracted repeatedly with petroleum (b. p. 80—100°) and on cooling the solution an oil separated which after repeated extractions solidified in small, pale yellow needles, m. p. 98—99° (Found : C, 56·9; H, 4·9; Se, 26·7. $C_{14}H_{14}O_2Se$ requires C, 57·3; H, 4·8; Se, 27·0%).

When boiled with concentrated hydriodic acid, the dihydroxyditolyl selenide readily decomposed with elimination of black selenium and production of 5-iodo-*o*-cresol (m. p. 72°).

Although insoluble in water, this complex selenide dissolved readily in either aqueous caustic soda or the common organic solvents. Concentrated sulphuric acid gave a deep green tint even in the cold.

3. p-*Cresol and Selenium Oxychloride.*—*p*-Cresol (67·2 g.; 3 mols.), dissolved in 500 c.c. of chloroform, was treated with selenium oxychloride (33·2 g.; 1 mol.) diluted with 50 c.c. of the same solvent. The well-stirred mixture slowly assumed a deep red colour, hydrogen chloride was evolved and selenonium chloride separated. The mixture was refluxed, and the precipitate washed with acetone and ether (yield, 17·5 g.). After crystallisation from hot alcohol and drying in a vacuum desiccator, the selenonium chloride retained alcohol of crystallisation which was removed at 110° (Found : C, 57·85; H, 6·0; Cl, 7·1; Se, 15·45; loss on heating at 110°, 14·4. $C_{21}H_{21}O_3ClSe,1\frac{1}{2}C_2H_6O$ requires C, 57·0; H, 6·0; Cl, 7·0; Se, 15·7;

loss, 13·7%). This preparation gave the iodoform reaction with iodine in aqueous caustic soda.

Tri-2-hydroxytri-5-methyltriphenylselenonium chloride (XI), which decomposed at 260—265°, was insoluble in water but dissolved in hot alcohol or in aqueous caustic soda. Concentrated sulphuric acid developed no coloration in the cold but, on warming, an olive-green tint changing to deep red. Alcoholic ferric chloride gave a faint olive-green tint. The corresponding complex *oxide* (XII), a white, amorphous powder, decomp. 160°, was precipitated by carbon dioxide or dilute acetic acid from an alkaline solution of the foregoing chloride (Found: Se, 19·1. $C_{42}H_{42}O_7Se_2$ requires Se, 19·4%). With bromine water this complex oxide was readily decomposed, yielding 3 : 5-dibromo-*p*-cresol (m. p. 48°).

Tri-3-bromotri-2-hydroxytri-5-methyltriphenylselenonium bromide (XIII), obtained by the action of anhydrous bromine on the oxide in the manner employed for the analogue from *o*-cresol, separated from hot alcohol in pinkish-white prisms, decomp. 195° (Found: Br, 45·0. $C_{21}H_{18}O_3Br_4Se$ requires Br, 44·6%).

Di-2-hydroxydi-5-methyldiphenyl selenide (XIV). The chloroform filtrate from the selenium oxychloride condensation after separation of the selenonium chloride was evaporated nearly to dryness and distilled in steam. The distillate contained 3-chloro-*p*-cresol (b. p. 196°/760 mm.; yield, 12·0 g.). The dried residue was extracted repeatedly with petroleum (b. p. 40—60°). Repeated crystallisation of the extracted material yielded the white *selenide*, m. p. 111° (Found: C, 57·0; H, 4·8; Se, 26·9. $C_{14}H_{14}O_2Se$ requires C, 57·3; H, 4·8; Se, 27·0%).

This complex aromatic selenide, although insoluble in water, dissolved readily in the common organic solvents. Cold concentrated sulphuric acid gave a deep green tint, becoming red on warming; alcoholic ferric chloride developed a deep green coloration. Concentrated hydriodic acid eliminated selenium from the selenide and yielded 3-iodo-*p*-cresol (m. p. 37—38°).

5-Chloro-4 : 4′-dihydroxy-3 : 3′-ditolyl (XVI). This singular by-product separated from the last fractions of the foregoing diaryl selenide in yellow clumps and after crystallisation from petroleum was obtained as a white, crystalline powder, m. p. 129—130° (yield, about 1 g.) [Found: C, 67·9; H, 4·85; Cl, 13·9; *M* (in camphor), 254·7. $C_{14}H_{13}O_2Cl$ requires C, 67·6; H, 5·3; Cl, 14·3%; *M*, 248·5].

4. *Resorcinol and Selenium Oxychloride.*—Resorcinol (33 g.; 3 mols.), suspended in 1000 c.c. of chloroform or dissolved in glacial acetic acid, was treated with selenium oxychloride (16·6 g.; 1 mol.) diluted with 100 c.c. of the same solvent. Each drop of the oxy-

chloride produced a transient green tint and a white precipitate separated. The solid portion of the jelly-like mixture was pressed and dissolved in acetone. On evaporation this solution yielded a selenonium chloride as a white powder. This product was dissolved in alcohol, and a large volume of acetone added; the selenonium chloride then separated slowly with acetone of crystallisation (1 mol.). With ammoniacal iodine the chloride yielded iodoform, thus confirming the presence of acetone. The substance melted at 206° (yield, 30 g.) (Found: C, 49·4; H, 4·5; Cl, 7·0; Se, 16·1; loss on heating at 110°, 12·1. $C_{18}H_{15}O_6ClSe,C_3H_6O$ requires C, 50·4; H, 4·2; Cl, 7·1; Se, 15·8; loss, 11·6%).

Tri-2 : 4-dihydroxytriphenylselenonium chloride (XVII) dissolved in boiling water to a pale red solution which set to a jelly on cooling. It also dissolved readily in alcohol or aqueous caustic soda but was only sparingly soluble in acetone or glacial acetic acid and insoluble in chloroform or benzeue. Aqueous ferric chloride developed a reddish-purple coloration, warm concentrated sulphuric acid gave a green tint, and bromine water decomposed this selenonium chloride completely.

5. *β-Naphthol and Selenium Oxychloride.*—Selenium oxychloride (16·6 g.; 1 mol.), diluted with 100 c.c. of chloroform, was stirred into 43·2 g. of β-naphthol (3 mols.) in 700 c.c. of this solvent. The mixture became warmer and darker and finally almost solid owing to the separation of organic selenide (yield, 35 g.). This product crystallised from acetone in lustrous, colourless prisms, melting at 186° to a red liquid (Found: C, 65·5; H, 3·65; Se, 22·0. $C_{20}H_{14}O_2Se$ requires C, 65·7; H, 3·9; Se, 21·7%).

Although insoluble in chloroform, benzene, ether, or water, *di-2-hydroxydi-1-naphthyl selenide* (XVIII) dissolved readily in acetone and sparingly in hot alcohol or glacial acetic acid. Cold concentrated sulphuric acid developed a green tint, but alcoholic ferric chloride had no colour effect. This complex selenide dissolved readily in aqueous caustic alkalis and was reprecipitated unchanged by acids. Evaporation of the chloroform filtrate from di-2-hydroxydi-1-naphthyl selenide and distillation in steam of the red residue gave 17 g. of 2-chloro-β-naphthol (m. p. 70°).

6. *Salicylic Acid and Selenium Oxychloride.*—Salicylic acid (41·4 g.; 3 mols.) and selenium oxychloride (16·6 g.; 1 mol.) were heated and stirred in an open basin so long as hydrogen chloride was evolved and until the yellow mixture had assumed a brown tint. After cooling, the hard product was powdered and extracted with hot benzene to remove ill-defined by-products, unchanged salicylic acid and 5-chlorosalicylic acid (m. p. 166—167°). The pale yellow residue (20 g.) was crystallised repeatedly from aqueous

alcohol, *disalicylyl selenide* (*di*-4-*hydroxydiphenyl selenide di*-3-*carboxylic acid*, XIX) being obtained in small, yellowish-white, micaceous plates, sintering at 250° and decomposing at 272° (Found : C, 47·4; H, 2·9; Se, 23·2. $C_{14}H_{10}O_6Se$ requires C, 47·5; H, 2·85; Se, 22·4%). Although readily soluble in alcohol, ether, acetone, or glacial acetic acid, the disalicylyl selenide is insoluble in water, chloroform, or benzene. It dissolved readily in aqueous caustic or carbonated alkalis. The very soluble sodium salt was precipitated by ether from alcoholic solution as a hygroscopic precipitate, becoming green on exposure. Cold concentrated sulphuric acid and the selenide developed a green coloration which deepened on warming. Ferric chloride and an alcoholic solution of the selenide gave an intense bluish-violet coloration.

Experiments on the condensation of selenium oxychloride with *m*-cresol, α-naphthol, and 2-hydroxy-3-naphthoic acid failed to furnish well-defined products.

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CCCCXXXVIII.—*The Electrical Conductivities of Some Uni-univalent Salts in Benzonitrile. Evidence for the Incomplete Dissociation of Strong Electrolytes and the Applicability of the Law of Mass Action to their Dissociation.*

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IN view of Debye and Hückel's theory and its recent developments, considerable significance attaches to the study of the conductivity of salts in non-aqueous solution. The earlier relevant data cannot be regarded as trustworthy, and it is only within the last few years that satisfactory measurements of conductivity in non-aqueous solution have been recorded (see Kraus and Bishop, *J. Amer. Chem. Soc.*, 1922, **44**, 2206; Morgan and Lammert, *ibid.*, 1924, **46**, 1117; Philip and Oakley, J., 1924, **125**, 1189; Frazer and Hartley, *Proc. Roy. Soc.*, 1925, *A*, **109**, 351; Walden, Ulich, and Laun, *Z. physikal. Chem.*, 1925, **114**, 275; Walden, Ulich, and Busch, *Z. physikal. Chem.*, 1926, **123**, 429). The present investigation was undertaken with the object of providing additional accurate data in this field, more especially over a wide range of temperature (compare Philip and Oakley, *loc. cit.*; Walden, *loc. cit.*). Benzonitrile was chosen as solvent because (1) it is easily purified, (2) it is inert and not hygroscopic, and (3) its b. p. is fairly

high. Moreover, it is desirable to examine a solvent less closely related to water than the alcohols which have been used in most of the accurate conductivity measurements in non-aqueous solutions. As solutes, potassium, sodium, and lithium iodides, lithium bromide, and silver nitrate were employed. The solubility of inorganic uni-univalent salts in benzonitrile is, with the exception of silver nitrate, not great, and the above are the only salts sufficiently soluble for the purpose. Among previous work on conductivities in benzonitrile, mention may be made of that of Walden on tetraethyl- and tetrapropyl-ammonium iodides (*Z. physikal. Chem.*, 1906, **54**, 189; **55**, 710) and of Dutoit on sodium iodide (*Z. Elektrochem.*, 1906, **12**, 643), all at 25°. The value of Λ_0 found by the author for sodium iodide at 25° is some 10% lower than Dutoit's, and the author's results yield a value for the mean ionic radius calculated from the Debye–Hückel theory of $3{\cdot}72 \times 10^{-8}$ cm., whereas Dutoit's give one of $6{\cdot}30 \times 10^{-8}$ cm.

EXPERIMENTAL.

Apparatus.—The bridge was set up as in the usual Wheatstone arrangement, the source of the current being connected to the sliding contact and the junction of the standard resistance with the cell. The sliding contact was earthed.

The bridge wire was of the drum type, 5 metres long, of 32 ohms resistance, and having an ebonite hood, made by Leeds and Northrup; it was calibrated by the method of Strouhal and Barus and had no appreciable error. The standard resistance was of the dial pattern, maximum resistance 11,110 ohms, accurate to 0·04%, made by Cambridge and Paul. The telephone was of 120 ohms resistance, made by Brown. The source of current was a valve oscillator made by the author and giving a pure sine-wave alternating current of frequency 1000 cycles per second. It was electromagnetically shielded from the bridge.

The condensers placed in parallel with the standard resistance in order to balance the capacity of the cell were (i) a step-up mica condenser of maximum capacity 1·0 microfarad, and (ii) a variable air condenser, of maximum capacity 0·001 microfarad, for fine adjustment: usually the air condenser alone sufficed.

The cells. Of the three cells used, two, one of lead glass and one of Pyrex (Cells P I and P II), were of the pipette type designed on the lines laid down by Washburn (*J. Amer. Chem. Soc.*, 1916, **38**, 2431). The platinum electrodes (3 cm. in diameter and 0·5 cm. apart) were grey-platinised. The capacity of each cell was about 20 c.c. The third cell (Cell III) was a stoppered, round-bottomed, Pyrex-glass bottle of about 20 c.c. capacity, the electrodes—two

grey-platinised platinum discs 1 cm. in diameter and about 1 cm. apart—being sealed in through the sides. The cell constants of the pipette cells were 0·034014 and 0·041729, and of the other cell 0·19057. The pipette cells were used for all except the most concentrated solutions, since with small electrodes satisfactory minima were not obtained with solutions of low conductivity (compare Washburn, *loc. cit.*).

Temperature Control.—The thermostats were controlled by mercury–toluene gas-regulators and were constant to $\pm$ 0·01°. A layer of oil was placed on the surface of those at temperatures of 50° and above. The bath at 0° was maintained with distilled water and ice which had been washed with distilled water.

Determination of Cell Constants.—The constant of Cell III was determined at 25° with an N/100-potassium chloride solution prepared according to Parker and Parker (*J. Amer. Chem. Soc.*, 1924, **46**, 312). The flask and small weighing bottle used were of hard glass and were steamed out before use. The water had a specific conductivity of 1×10^{-6} mho. The potassium chloride (A.R. quality) was recrystallised twice from conductivity water, fused in a platinum dish, and ground in an agate mortar. Two samples were prepared and both led to the same result for the cell constant. The constants of the two pipette cells could not be determined with this solution, since its conductivity was great enough to be outside the range of satisfactory minima. They were therefore obtained by intercomparison with Cell III. All three cells were filled with a solution consisting of 100 c.c. of N/100-potassium chloride and 900 c.c. of alcohol (Morgan and Lammert, *J. Amer. Chem. Soc.*, 1923, **45**, 1692); the ratio of the resistance of the cells so filled was the ratio of their cell constants, and, the constant of one of them being known, those of the others were readily calculated.

The ratio of the cell constants was found to be the same at all the temperatures used, and, since the dimensions of the pipette cells and Cell III were very different, this indicates that the constants of all of them were not appreciably altered by temperature. The values of the cell constants determined at 25° were therefore used for all the temperatures investigated; they were redetermined at frequent intervals and were found not to alter appreciably, except that of Cell P I which changed a little in the first month or so after manufacture.

Preparation of the Salt Solutions.—The solutions were made in 50 or 100 c.c. flasks with ground stoppers. If they were to be kept for any length of time, the stopper was covered by a cap and waxed. The flasks were specially selected not to have capillaries which might retain water. After thorough cleaning, they were washed

repeatedly with conductivity water and then with redistilled absolute alcohol and placed upside-down in a steam oven to dry. They were rapidly removed to a desiccator containing phosphoric oxide, the desiccator was evacuated, and purified, dry air was admitted after the flasks had cooled.

All the solutions were made up by weight. The weight of dissolved salt was subtracted from the weight of solution, and from the resulting weight of pure solvent and the density of pure benzonitrile at the appropriate temperature the volume concentrations were calculated, *i.e.*, electrostriction was taken to be negligible. This assumption was found to be justified in the case of an $N/100$-silver nitrate solution, which was the highest concentration used.

The densities of benzonitrile at temperatures between 0° and 70° were found to be as follows :

Temp. ...	0°	25°	40°	50°	55°	70°
$d_{4^\circ}^{t^\circ}$	1·0222	1·0005	0·9872	0·9778	0·9739	0·9600

The stock solution was made by adding to a weighed amount of benzonitrile a small weighing bottle containing a weighed amount of the salt and shaking until the salt had dissolved. Potassium iodide was exceptionally slow in dissolving and sometimes had to be shaken over-night. The quantity of salt taken was of the order of 0·05—0·1 g. and was weighed to 0·01 mg., the method of oscillations being used.

The more dilute solutions were made by adding to flasks containing a weighed quantity of benzonitrile the requisite quantity of a more concentrated solution and weighing again. The weights were not reduced to *vacuo* since the same percentage error occurs both in the weight of pure solvent and in the weight of the previous dilution added, the resultant error being zero. No dilute solution was derived from a stronger solution which had previously been used for any other purpose. All the transferences were carried out in pipettes which had been cleaned and dried in the same way as the flasks, except that instead of cooling them in a vacuum desiccator, a stream of purified and dry air was drawn through them. When not in use, the ends of the pipettes were closed with rubber caps in order to prevent access of moist air. No pipette was used more than once in a series of dilutings, and a suitable guard was inserted between the mouth and the pipette. Experiment showed that the pouring of benzonitrile from one vessel to another in an ordinary room did not noticeably alter its conductivity.

Whetham's method of preparing solutions for conductivity measurements (*Phil. Trans.*, 1900, *A*, **194**, 321), in which successive portions of a concentrated salt solution are added from a weight pipette to a known volume of pure solvent in the cell, was inapplic-

able in the present work for the following reasons: (1) As will be explained later, it was necessary for the cell to have been filled with a concentrated solution before the more dilute solutions were measured. (2) Most of the salts investigated were so sparingly soluble in benzonitrile that large volumes of a stock solution would have had to be added in order to obtain the more concentrated solutions, thereby altering the effective constant of the cell.

The method used in the present work has none of the defects of the Ostwald–Arrhenius method, except the slight uncertainty as to the magnitude of the solvent correction.

Conductivity Measurements.—Before a series of measurements, the cells were cleaned with chromic–sulphuric acid mixture, washed with conductivity water, and warmed several times with conductivity water. They were then washed thoroughly with redistilled absolute alcohol and dried by being warmed to about 80° and having a current of purified dry air drawn through them. Cell III was dried by leaving it in a steam-oven and then allowing it to cool in a vacuum desiccator in the same way as the flasks used in making up the solutions. Between individual measurements in a single series of dilutions, the method of washing and drying the cell was the same, except that treatment with cleaning mixture and water was omitted. As recommended by Morgan and Lammert (*loc. cit.*, 1923), the electrodes were kept short-circuited during the process of cleaning and drying.

During the conductivity measurements, the bridge was approximately set and the current switched off for a minute; the fine setting was then made in about two seconds. This procedure was adopted in order to avoid errors due to the heating effect of the current. Perfect minima were always obtained, and the bridge could be set to 0·01% of its length.

With each salt at least two series of measurements starting from different stock solutions were made.

In the case of potassium iodide, a photochemical reaction took place which resulted in a minimum in the equivalent conductivity at high dilutions, but this was avoided by painting the cell with Brunswick black. It was also found that the conductivity of dilute potassium iodide solutions was not constant if the measurements were carried out beginning with the most dilute solution and working up to the most concentrated. If the measurements proceeded in the reverse order the conductivities were quite constant. This phenomenon was traced to adsorption on the electrodes. On *immersion in a concentrated solution, an amount of electrolyte is* adsorbed the removal of which does not noticeably alter the conductivity of the solution. The amount of adsorbed electrolyte does

not vary appreciably with its concentration in the solution, and consequently in the more dilute solutions the electrolyte is neither further adsorbed on the electrodes nor given up to the solution. This latter point was proved by measuring the conductivity of the pure solvent in the cell, and then filling it with a concentrated solution, washing it in the way usual between two measurements, and measuring the conductivity of the pure solvent again. The two values thus obtained were identical. This observation is in agreement with the experience of Randall and Scott (*J. Amer. Chem. Soc.*, 1927, **49**, 636), who, in investigating the variation of cell constant with resistance and other factors, found that the quantity of electrolyte adsorbed did not vary appreciably with the concentration of the surrounding solution. All the measurements were therefore carried out in the dark and (except in the case of silver nitrate, where no trouble was experienced) beginning with the most concentrated solution and proceeding to the most dilute.

Solvent Correction.—The conductivity of the solvent was in all cases subtracted from the observed conductivity in order to obtain the conductivity due to the dissolved salt. The correction never amounted to more than 4%, and satisfactory agreement between the values for the conductivity of the dissolved salt was obtained even when the conductivity of the pure solvent varied by 100%, provided it did not exceed $1\cdot0 \times 10^{-7}$ mho.

Since the viscosity of an $N/100$-silver nitrate solution was the same as that of the pure solvent, it was unnecessary to apply a viscosity correction.

The molecular weights of the salts concerned have been taken as: potassium iodide 166·02; sodium iodide 149·92; lithium iodide 133·86; lithium bromide 86·86; silver nitrate 169·89.

Purification of Materials.—Benzonitrile. Benzonitrile (B.D.H.) was steam-distilled to remove the slight amount of carbylamine present. The distillate was washed with sodium carbonate to remove any benzoic acid, the benzonitrile extracted with ether, and the extract washed with water and dried over calcium chloride. After filtering, the ether was distilled off and the residue distilled under low pressure. The large middle fraction, b. p. 81°/22 mm., was then subjected to the following operations, being redistilled under diminished pressure after each: (1) shaken slowly with a mixture of anhydrous potassium carbonate and calcium chloride and filtered; (2) shaken very slowly with calcium chloride and decanted; (3) left over calcium chloride for some days and decanted. The benzonitrile then had a specific conductivity of $0\cdot5 \times 10^{-7}$ mho at 25°. Between two series of measurements it was treated as above, except that the steam-distillation was omitted. The

distilling apparatus was washed with redistilled absolute alcohol an dried in the same way as the flasks used in making up the solution

Potassium and sodium iodides. The A.R. quality salts wei recrystallised from conductivity water in a platinum basin and drie Finally they were powdered in an agate mortar and electricall heated in a vacuum to 100° over phosphoric oxide, the drying ager remaining at room temperature. Analysis of the potassium iodid gave 76·4% iodine (calc., 76·4%), and of the sodium iodide 84·6% (calc., 84·7%). The sodium iodide did not turn at all yellow o keeping.

Lithium iodide. A sample of Kahlbaum's lithium iodide wa slightly pink and contained free alkali. It was evaporated t dryness with freshly prepared hydriodic acid at about 50° in a electrically heated beaker in a desiccator containing caustic potasl and then recrystallised thrice from redistilled absolute alcohol. It was perfectly colourless, gave no blue colour with starch, and it aqueous solution was neutral. The salt was dried by heating in small hard-glass weighing bottle to 120° in the apparatus used fc drying the potassium and sodium iodides and evacuating cor tinuously for a week. In order to avoid transference of the ver hygroscopic anhydrous lithium iodide, the weighing bottle wa weighed empty, and the requisite amount of the damp salt adde and dried as described above. The cap of the weighing bottle wa then dropped on to it with a pair of forceps as it stood in th desiccator, and the covered bottle was removed, weighed, an dropped into a weighed quantity of pure benzonitrile to make u the stock solution. The material so prepared gave 94·7% iodir (calc., 94·8%), and contained no detectable alkali or free iodine.

Lithium bromide. The B.D.H. product, which was quite colourle and free from alkali, was recrystallised three times from redistille absolute alcohol, and dried in the same way as the lithium iodid (Found: Br, 92·2. Calc., Br, 92·0%).

Silver nitrate. This was kindly provided by Dr. H. F. Harwoo and had been purified for atomic-weight purposes. It was drie in the same way as the potassium iodide.

Alcohol. The absolute alcohol used for washing was redistilled i order to remove any electrolytic or high-boiling impurities.

Results.

The results of the conductivity measurements are given i Table I, v denoting the dilution (in litres). In the column headed .

* Since lithium iodide is very soluble in alcohol, recrystallisation fro this solvent is wasteful, and an attempt was made to precipitate it by th addition of ether, in which it is insoluble; but the liquid separated into tw phases, one chiefly ether and the other a solution of lithium iodide in alcohol

TABLE I.

Results of Conductivity Measurements.

	Series.	v.	Λ.	Δ.	Δ'.
KI, 0°.	d	803·1	27·50	+0·01	−0·05
	c	1,160	28·42	−0·01	±0·00
	d	2,078	29·61	+0·01	+0·08
	c	4,446	30·56	−0·01	+0·01
	d	7,639	31·00	±0·00	−0·06
	d	20,045	31·31	−0·13	−0·41
KI, 25°.	a	802·4	42·82	±0·00	−0·01
	b	907·2	43·39	+0·01	±0·00
	c	1,185	44·40	−0·05	−0·07
	a	3,256	47·60	±0·00	+0·08
	c	4,543	48·30	±0·00	+0·08
	b	8,806	49·29	+0·01	−0·03
	a	14,774	49·70	−0·08	−0·25
	a	39,188	50·45	+0·08	−0·34
KI, 40°.	a	813·2	52·64	+0·01	−0·01
	b	919·5	53·32	±0·00	−0·06
	c	1,201	54·67	−0·02	−0·13
	a	3,300	58·84	+0·01	+0·05
	c	4,604	59·83	+0·03	+0·11
	b	8,924	61·14	−0·02	−0·02
	a	14,973	61·60	−0·21	−0·40
	a	39,712	62·34	−0·06	−0·74
KI, 55°.	a	824·2	62·81	+0·01	±0·00
	b	932·0	63·60	±0·00	−0·45(?)
	c	1,218	65·39	−0·01	−0·16
	a	3,345	70·66	±0·00	+0·07
	c	4,667	71·86	+0·03	+0·11
	b	9,046	73·49	±0·00	−0·08
	a	15,177	74·09	−0·17	−0·53
	a	40,254	75·01	+0·05	−1·00
KI, 70°.	d	855·2	72·94	±0·00	±0·00
	c	1,235	76·09	+0·01	−0·06
	d	2,212	80·35	+0·01	+0·20
	c	4,734	83·95	−0·02	+0·05
	d	8,134	85·72	+0·02	−0·08
NaI, 0°.	b	466·5	24·40	+0·05	—
	a	474·2	24·39	±0·00	—
	c	508·3	24·55	−0·02	—
	a	876·8	25·82	−0·01	+0·05
	b	1,668	27·06	−0·01	±0·00
	a	5,270	28·56	+0·02	+0·01
	b	8,180	28·88	−0·02	−0·04
	c	17,450	29·28	±0·00	−0·13
	a	32,142	29·45	±0·00	−0·23
	a	59,488	29·46	−0·04	−0·42
NaI, 25°.	b	476·6	37·79	−0·05	—
	a	484·5	37·98	±0·00	—
	c	519·4	38·50	+0·05	—
	a	895·8	40·99	−0·01	−0·10
	b	1,704	43·03	−0·01	±0·00
	a	5,384	45·29	±0·00	+0·04
	b	8,358	45·85	+0·02	+0·03
	c	17,830	46·46	−0·01	−0·08
	a	32,841	47·01	+0·20	+0·05
	a	60,781	46·97	±0·00	−0·28

TABLE I (*contd.*).

	Series.	v.	Λ.	Δ.	Δ′.
NaI, 50°.	b	487·7	51·57	+0·01	—
	a	495·7	51·65	−0·01	—
	c	531·4	52·26	±0·00	—
	a	916·6	56·57	−0·04	−0·60
	b	1,744	60·23	±0·00	±0·00
	a	5,509	63·82	+0·01	+0·08
	b	8,551	64·57	±0·00	−0·09
NaI, 70°.	b	496·7	62·25	±0·00	—
	a	504·9	62·50	−0·01	—
	c	541·2	63·45	−0·04	—
	a	933·6	69·73	−0·02	−0·84
	b	1,776	74·42	+0·01	±0·00
	a	5,611	78·87	±0·00	±0·00
	b	8,710	80·35	+0·44	+0·66
LiI, 0°.	a	100·9	15·37	±0·00	—
	b	492·9	21·20	±0·00	±0·00
	a	923·3	23·27	−0·03	−0·30
	b	2,290	25·90	+0·01	−0·02
	a	4,549	27·10	±0·00	±0·00
	a	9,178	27·91	+0·05	−0·01
	b	9,513	27·70	−0·22	−0·28
LiI, 25°.	a	103·1	24·91	±0·00	—
	b	503·6	34·56	±0·00	−0·14
	a	943·3	38·14	−0·01	+0·04
	b	2,340	41·72	+0·03	+0·24
	a	4,648	43·18	−0·07	−0·01
	a	9,164	44·37	+0·11	±0·00
	b	9,719	44·00	−0·32	−0·46
LiI, 50°.	a	105·4	34·73	±0·00	—
	b	515·3	48·83	±0·00	−0·07
	a	965·2	53·82	−0·02	+0·01
	b	2,394	58·85	+0·03	+0·23
	a	4,756	60·88	−0·10	−0·17
	a	9,377	62·74	+0·45	−0·01
	b	9,945	61·97	−0·46	−0·89
LiBr, 0°.	a	487·5	7·10	−0·07	—
	c	552·6	7·52	+0·03	—
	a	982·8	9·39	+0·05	—
	b	1,949	12·15	−0·07	±0·00
	a	4,836	16·14	−0·01	−0·05
	b	8,146	17·85	+0·01	+0·03
	a	9,899	18·50	+0·13	+0·17
LiBr, 25°.	a	498·1	11·38	−0·02	—
	c	564·6	11·92	+0·03	—
	a	1,004	14·70	−0·06	—
	b	1,992	19·49	+0·03	±0·00
	a	4,941	25·47	−0·10	−0·13
	b	8,323	28·17	+0·04	+0·12
	a	10,114	29·25	+0·19	+0·45
LiBr, 50°.	a	509·7	15·52	−0·05	—
	c	577·7	16·39	+0·06	—
	a	1,027	20·16	+0·01	—
	b	2,038	27·33	+0·06	±0·00
	a	5,056	35·25	−0·10	−0·38
	b	8,516	39·24	+0·08	+0·26
	a	10,349	40·77	+0·40	+0·75

TABLE I (*contd.*).

	Series.	v.	Λ.	Δ.	Δ'.
LiBr, 70°.	a	519·1	18·72	±0·00	—
	c	588·4	19·85	+0·05	—
	a	1,046	24·55	±0·00	—
	b	2,076	32·51	+0·20	±0·00
	a	5,149	43·33	−0·37	−0·35
	b	8,674	48·44	+0·18	+0·34
	a	10,540	50·33	+0·58	+0·83
$AgNO_3$, 0°.	c	39·10	4·98	±0·00	—
	c	78·2	6·62	+0·05	—
	b	91·22	7·26	+0·35(?)	—
	a	104·6	7·07	−0·13	—
	c	156·4	8·12	−0·08	—
	a	598·0	13·60	−0·13	—
	b	709·2	14·92	+0·10	—
	a	3,119	22·46	+0·08	±0·00
	b	7,398	25·56	−0·07	−0·58
	a	11,432	27·58	+0·40	−0·01
	a	21,504	29·17	+0·05	+0·04
	a	40,400	30·11	−0·44	−0·11
$AgNO_3$, 25°.	c	39·86	7·50	−0·18	—
	c	79·72	9·86	+0·09	—
	b	93·20	10·55	+0·25	—
	a	106·8	10·62	−0·15	—
	c	159·4	12·30	−0·05	—
	a	611·0	20·57	−0·23	—
	b	724·6	22·18	+0·01	—
	a	3,276	34·72	+0·13	±0·00
	b	7,559	40·17	−0·16	−0·54
	a	11,680	42·88	−0·03	−0·09
	a	21,972	45·79	+0·08	+0·31
	a	41,278	47·28	±0·00	−0·01
$AgNO_3$, 40°.	b	94·46	12·48	+0·10	—
	a	108·3	12·77	−0·10	—
	a	619·2	24·75	−0·02	—
	b	734·3	26·49	+0·09	—
	a	3,320	41·92	+0·22	±0·00
	b	7,661	49·39	−0·26	−0·36
	a	11,837	52·83	−0·06	−0·13
	a	22,267	56·69	+0·45	+0·69
	a	41,833	58·07	−0·47	−0·30
$AgNO_3$, 55°.	b	95·75	14·36	+0·03	—
	a	109·7	14·90	−0·04	—
	a	627·7	28·91	−0·01	—
	b	744·4	30·73	−0·17	—
	a	3,365	49·48	+0·08	±0·00
	b	7,765	58·82	−0·03	+0·20
	a	11,999	62·98	+0·15	+0·32
	a	22,571	67·70	+0·63	+0·97
	a	42,404	68·62	−0·86	−1·03

are the differences between the observed points and a smooth curve drawn through them on a Λ–log c graph. Since the equation of this smooth curve is, except for the most concentrated solutions and for lithium bromide and silver nitrate, $\Lambda_0 = \Lambda + ac^n$, a and n being determined by Ferguson and Vogel's method (*Phil. Mag.*, 1925, **1**, 971), these differences are also the differences between the

observed values and those calculated from this equation. Under Δ' are the differences between the observed points and a straight line drawn through them on a plot of Λ against $\sqrt{c}$, a positive sign before Δ indicating that the observed point is above the curve.

The values of the equivalent conductivity at even dilutions are given in Table II. Interpolation was carried out on a Λ–$\log c$ graph drawn with a flexible spline.

TABLE II.

Temp.	0°.	25°.	40°.	55°.	70°.	0°.	25°.	50°.	70°.
v.			Λ.					Λ.	
		Potassium Iodide.					Sodium Iodide.		
500	—	—	—	—	—	24·54	38·17	51·74	62·33
1,000	28·06	43·77	53·76	64·08	74·31	26·10	41·41	57·20	70·36
2,000	29·54	46·31	57·10	68·38	79·70	27·36	43·43	60·82	75·06
5,000	30·67	48·46	60·00	72·03	84·18	28·50	45·17	63·60	78·57
10,000	31·18	49·41	61·33	73·67	86·23	29·05	46·01	64·80	80·22
20,000	—	50·01	—	—	—	29·33	46·54	—	—
50,000	—	50·46	—	—	—	29·49	46·96	—	—
		Silver Nitrate.					Lithium Iodide.		
50	5·55	8·36	—	—	—	—	—	—	—
100	7·10	10·51	12·57	14·50	—	15·36	24·73	34·25	—
500	12·72	19·26	22·83	26·57	—	17·88	34·54	48·57	—
1,000	16·83	24·73	29·37	34·45	—	23·57	38·45	54·10	—
2,000	20·35	30·55	36·42	42·97	—	25·57	41·22	58·08	—
5,000	24·15	37·60	45·69	54·09	—	27·23	43·38	61·09	—
10,000	26·71	42·00	51·73	61·30	—	27·96	44·35	62·38	—
20,000	28·91	45·37	—	—	—	—	—	—	—

Temp.	0°.	25°.	50°.	70°.
v.		Λ.		
		Lithium Bromide.		
500	7·23	11·42	15·46	18·43
1,000	9·40	14·73	19·92	24·13
2,000	12·34	19·92	27·08	31·78
5,000	16·27	25·62	35·28	43·42
10,000	18·40	29·00	40·22	49·34

Viscosity Measurements.—An Ostwald viscometer was used. The measurements were made in a glass-sided thermostat, the temperature of which was constant to ± 0·01°. Drying tubes, attached to both ends of the viscometer, were found to be without effect on the time of flow. The viscometer was cleaned with alcohol and nitric acid, washed with water and alcohol, and dried in a warm bath by a current of purified dry air which was filtered from all dust particles by means of a Jena-glass filter. All the wash liquids and liquids to be measured were filtered similarly, since this method for removing dust motes has been found to be both convenient and very efficient. The time of flow was never less than 300 seconds,

ınd readings were reproducible to $\frac{2}{5}$ sec. after emptying, cleaning, lrying, and refilling the viscometer.

A correction was applied for the error at higher temperatures, ırising from the fact that the coefficient of expansion of benzo- ıitrile *is greater* than that of water, and hence that, whilst the rolumes of benzonitrile and water placed in the viscometer were equal at the temperature at which they were measured, *viz.*, room emperature, they were not equal at other temperatures. The extra time of flow at 40° due to an additional 1 c.c. of water was letermined, and, the effect of 1 c.c. of a liquid of a certain density being known, the effect of any volume of a liquid of any density could be calculated by simple proportion. The difference in rolume of the benzonitrile and water in the viscometer was calculated rom a knowledge of their densities at the temperatures involved, ınd the extra time of flow due to the larger volume of the benzo- ıitrile was subtracted from its observed time of flow. The correc- ion never amounted to more than 0·75% and averaged about 0·25%. The viscometer had previously been found by H. B. Oakley, of this lepartment, to have a negligible deviation from Poiseuille's law. The values adopted for the viscosity of water were those of Bingham ınd White (1912).

The results obtained for the viscosity of benzonitrile at various emperatures were:

'emp.	0°	25°	40°	50°	55°	70°
$\times 10^4$	194	124	100	87·6	82·6	66·6

Extrapolation to Λ_0.—Of the numerous formulæ that have been proposed for extrapolation to the equivalent conductivity at zero concentration (Λ_0) only two need now be considered.

(1) Kohlrausch's square-root law

$$\Lambda_0 = \Lambda + xc^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

s important since it has been theoretically deduced hy Debye and Hückel. The accuracy with which it applies to these benzonitrile olutions is illustrated hy the differences in the last column of Table I. The range of dilution over which this equation holds is or potassium iodide $N/1000$ to $N/10,000$; for sodium iodide up to . concentration of $N/1000$; for lithium iodide up to $N/500$; and or lithium bromide and silver nitrate up to $N/2000$. This range s the same at all the temperatures at which experiments were carried ut. In the case of potassium iodide at dilutions greater than 0,000 litres there is a definite deviation which may be due to experi- nental error. The values of Λ_0 and x obtained by this method re given in Table III, the unit of concentration being 1 g.-equiv. er litre.

TABLE III.

Values of Λ_0 and x (square-root law).

Temp.		0°.	25°.	40°.	50°.	55°.	70°.
KI	Λ_0 ...	32·76	52·12	64·83	—	78·22	91·95
	x	147·7	263·3	347·7	—	442·4	555·7
NaI	Λ_0 ...	30·45	48·11	—	68·28	—	84·58
	x	138·1	210·0	—	336·2	—	428·2
LiI	Λ_0 ...	29·98	47·33	—	66·99	—	—
	x	194·4	283·6	—	410·8	—	—
LiBr	Λ_0 ...	23·20	36·17	—	50·09	—	62·87
	x	488·0	744·5	—	1028	—	1380
$AgNO_3$	Λ_0 ...	33·30	52·18	64·78	—	77·50	—
	x	613·3	998·3	1318	—	1628	—

(2) Ferguson and Vogel's formula (*loc. cit.*)

$$\Lambda_0 = \Lambda + ac^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the best values of the constants a and n are determined by a graphical method, is logically the most satisfactory method of extrapolation. It has been applied except in the cases of silver nitrate and lithium bromide, where an equation of this form is not followed over a wide enough range to permit a satisfactory determination of a and n. In determining the constants in equation (2) the values of Λ at the series of concentrations (c) in geometrical progression were read off from plots of Λ against log c, instead of c, the latter being Ferguson and Vogel's practice. A common ratio of 1·5 was used. The range of concentration over which equation (2) is followed is for potassium iodide from the lowest concentrations measured up to $N/2000$, and for sodium and lithium iodides up to $N/1000$. The values of Λ_0 obtained from equation (2) and the values of the constants a and n are given in Table IV.

TABLE IV.

(Ferguson's method.)

	Values of Λ_0.			Values of n.			Values of a.		
Temp.	KI.	NaI.	LiI.	KI.	NaI.	LiI.	KI.	NaI.	LiI.
0°	32·15	30·51	29·29	0·632	0·484	0·634	320·6	125·3	456·4
25	51·11	47·57	45·99	0·637	0·600	0·658	607·8	396·3	710·7
40	63·83	—	—	0·615	—	—	723·6	—	—
50	—	66·79	64·38	—	0·687	0·711	—	1107	1397
55	76·73	—	—	0·626	—	—	978·4	—	—
70	89·98	82·34	—	0·631	0·726	—	1244	1805	—

The values to which both a and n appear to tend with increase of temperature for the iodides of the alkali metals are in the inverse order of atomic weight. At the lower temperatures there is no regularity, and that at the higher temperatures is perhaps merely fortuitous. This is in contrast with the finding of Ferguson and Vogel (*loc. cit.*, 1925) for electrolytes in water.

Discussion.

The Values of Λ_0.—For the iodides of the alkali metals Λ_0 increases with increasing atomic weight and volume. Frazer and Hartley (*loc. cit.*) observed the same phenomenon in methyl-alcoholic solutions. It must, therefore, be supposed that solvation or some form of interaction between solvent and solute occurs in these solvents as well as in water.

In Table V are given the ratios of the values of Λ_0 for the salts in benzonitrile at 25° to the corresponding values in water and methyl alcohol at 25°, and for potassium iodide at 0°, 25°, 40°, 55°, and 70° in benzonitrile to the values at the corresponding temperatures in nitromethane. The values in aqueous solution were obtained from the data of Kohlrausch ("Das Leitvermögen der Elektrolyte," 1916), in nitromethane from those of Philip and Oakley (*loc. cit.*), and in methyl alcohol from those of Frazer and Hartley (*loc. cit.*). In the last case, the values of Λ_0 of lithium iodide, lithium bromide, and sodium iodide were calculated from the ionic mobilities concerned, these salts not having been directly investigated. For the sake of consistency values of Λ_0 determined by the square-root law have been used throughout. The ratios of the viscosities of the solvents are also given.

TABLE V.

Solute.	Λ_0, PhCN.	Λ_0, H_2O.	Λ_0, MeOH.	$\frac{\Lambda_0,\ \text{PhCN}}{\Lambda_0,\ H_2O}$.	$\frac{\eta,\ H_2O}{\eta,\ \text{PhCN}}$.	$\frac{\Lambda_0,\ \text{PhCN}}{\Lambda_0,\ \text{MeOH}}$.	$\frac{\eta,\ \text{MeOH}}{\eta,\ \text{PhCN}}$.
KI	52·12	150·5	114·7	0·35		0·45	
NaI	48·11	127·0	106·7	0·38		0·45	
LiI	47·33	115·7	100·6	0·41	0·72	0·47	0·45
LiBr	36·17	117·1	95·1	0·31		0·38	
$AgNO_3$	52·18	133·8	112·9	0·39		0·46	

Values for potassium iodide in benzonitrile and nitromethane, and ratio of viscosities of solvents.

Temp.	Λ_0, PhCN.	Λ_0, $Me{\cdot}NO_2$.	$\frac{\Lambda_0,\ \text{PhCN}}{\Lambda_0,\ Me{\cdot}NO_2}$.	$\frac{\eta,\ Me{\cdot}NO_2}{\eta,\ \text{PhCN}}$.
0°	32·76	91·3	0·36	0·43
25	52·12	123·8	0·42	0·51
40	64·83	145·6	0·45	0·53
55	78·42	169·4	0·46	0·54
70	91·95	194·4	0·47	0·59

If the motion of the ions is in accordance with Stokes's law, and if the ions are the same size in each solvent, the ratio of the values of Λ_0 of a given salt in two solvents should equal the ratio of the fluidities (*i.e.*, the inverse ratio of the viscosities) of the solvents. This is so for benzonitrile and methyl alcohol, and approximately so for benzonitrile and nitromethane, but for benzonitrile and water the values of Λ in the former are about half as great as would be

expected from its viscosity. This can be explained by supposing that in the two non-aqueous solvents the extent of solvation or interaction between ion and solvent as suggested by Born (*Z. Physik* 1920, **1**, 221) is the same, and in both cases greater than in water. That in this respect benzonitrile resembles methyl alcohol and that both differ from water affords yet further evidence of the unique position of water amongst liquids.

The Variation of Λ_0 with Temperature.—If the logarithm of Λ_0 for a given salt at different temperatures is plotted against the logarithm of the fluidity of the solvent, an unequivocally straight line results, from the slope of which it is found that Λ_0 varies as the *m*th power of the fluidity, where *m* for potassium iodide is 1·01, for sodium iodide 0·99, for lithium iodide 1·00, for lithium bromide 0·97, and for silver nitrate 1·01. It is clear that within the limits of experimental error Λ_0 is directly proportional to the fluidity of the solvent, and the constancy of the product $\Lambda_0\eta$ for a given salt is clearly shown in Table VI, which gives values of Λ_0 at 10° intervals from 0° to 70°, and of the product $(\Lambda_0)_{t°}.\eta_{t°}$. The values of Λ_0 and η at temperatures at which they were not measured were interpolated graphically from plots of these quantities against temperature. Deviations from simple proportionality occur for all electrolytes at 60° and 70°.

TABLE VI.

	KI.		NaI.		LiI.		LiBr.		$AgNO_3$.	
Temp.	Λ_0.	$\Lambda_0\eta$.	Λ_0.	$\Lambda_0\eta$.	Λ_0.	$\Lambda_0\eta$.	Λ_0.	$\Lambda_0\eta$.	Λ_0.	$\Lambda_0\eta$.
0°	32·1	0·62	30·5	0·59	29·3	0·57	23·2	0·45	33·3	0·64
10	39·5	0·63	37·1	0·59	35·8	0·57	28·3	0·45	40·6	0·65
20	47·2	0·63	44·0	0·59	42·5	0·57	33·4	0·45	48·3	0·65
30	55·2	0·64	51·3	0·59	49·6	0·57	38·7	0·44	56·4	0·65
40	*63·6*	*0·64*	*58·9*	*0·59*	*56·8*	*0·57*	*44·2*	*0·44*	*64·8*	*0·65*
50	72·3	0·63	66·8	0·59	64·4	0·57	50·1	0·44	73·2	0·64
60	81·1	0·62	74·5	0·57	72·3	0·55	56·5	0·43	81·7	0·62
70	90·0	0·60	82·4	0·55	—	—	62·9	0·43	—	—

Comparison of the Results with the Theory of Debye and Hückel.

According to the theory of Debye and Hückel (*Physikal. Z.*, 1923, **24**, 305) there is, in dilute solutions of strong electrolytes, a linear relation between equivalent conductivity and the square root of the concentration. The author's results (with the exception of those for extremely dilute potassium iodide solutions, which may be in error) are in agreement with this theory in so far as they yield straight-line plots of Λ against $\sqrt{c}$, as demonstrated by the fact that there are as many positive as negative differences in the last column of Table I; but the agreement with the equation $\Lambda_c = \Lambda + ac^n$, where *n* is not 0·5, is still closer, as is evident from

a comparison of the last two columns of Table I. However, the mean differences from the square-root law (1 part in 400 parts) and from equation (2) (1 part in 1000 parts) are both near to the possible accidental error of the measurements, and in addition there is the possibility of a slight systematic error, the magnitude of which could not be estimated from the data themselves. The true value of the index n therefore remains in doubt, for the somewhat superior fit of equation (2), in which there is an additional adjustable constant, may represent not a law of nature but merely the experimental error of the measurements. A comparison of the ranges of concentration over which the rival equations hold leads to no conclusion, since this range is approximately the same for both and the square-root law, according to Debye's theory, cannot be expected to hold in concentrated solutions owing to the approximations made in its deduction. At this point exception must be taken to Ferguson and Vogel's practice of testing the fit of their equation by comparing the consistency of the values of Λ_0 calculated from it with that of those calculated from the square-root law, using in both cases rounded values of Λ read off from a plot of Λ against c, *i.e.*, from the curve whose equation is $\Lambda_0 = \Lambda + ac^n$. The consistency of the values of Λ_0 so determined from their equation is a measure, not of its agreement with experiment, but of the skill with which a curve of the form $\Lambda_0 = \Lambda + ac^n$ has been drawn and its constants determined. Equation (2) is therefore represented in an unduly favourable light.

A similar situation occurs in methyl-alcoholic solutions, and here the view that the deviation of n from 0·5 is due to experimental error is favoured by the fact that the values of Λ_0 calculated from equation (2) definitely do not agree with Kohlrausch's law of the independent migration of ions, the validity of which can hardly be doubted, as closely as those calculated from the square-root law (Frazer and Hartley, *loc. cit.*; Vogel, *Phil. Mag.*, 1928, **5**, 199). On the other hand, it is difficult to believe that, although in general the values of n are within 20% of 0·5, this deviation, in aqueous as well as in non-aqueous solution, is in every case due to experimental error. Furthermore, certain regularities have been found in the author's data, based on values of Λ_0 calculated from equation (2), which do not always occur if those yielded by the square-root law are used (see later).

The author inclines to the opinion that deviations from the square-root law are magnified when judged by the difference between the value of n in equation (2) and 0·5, but that when this difference is large and the data are accurate there is a departure from the theory of Debye and Hückel. From the foregoing, the

inadequacy both of plotting Λ against $\sqrt{c}$ and of determining n equation (2) as a test of Debye's theory is apparent, and as a m certain test the slope of the Λ–$\sqrt{c}$ line and its calculation fr the theory will now be considered.

The original Debye–Hückel theory (*loc. cit.*, p. 315) gives following derivation for the slope (x) of the straight line obtair by plotting Λ against $\sqrt{c}$ for uni-univalent electrolytes :

$$1 - f_\Lambda = (\Lambda_0 - \Lambda)/\Lambda_0 = (K_1 w_1 + K_2 b)\sqrt{2c} \quad . \quad . \quad (3$$

$$K_1 = \frac{\varepsilon F}{6DRT}\sqrt{\frac{4\pi F^2}{DRT \times 10^3}}; \qquad K_2 = \sqrt{\frac{4\pi F^2}{DRT \times 10^3}}$$

where ε = the elementary charge of electricity;
D = the dielectric constant of the solvent at T° (Abs.);
F = the value of the faraday ($= N\varepsilon$, where N = Avo dro's number);
R = the gas constant per g.-mol.;
$w_1 = \frac{1}{2}(l_a/l_c + l_c/l_a)$, where l_a and l_c are the mobilities the anion and kation, respectively;
and b = the mean radius of the anion and kation.

(The term K_1w_1 gives the diminution in conductivity due to dissymmetry of the ion atmosphere, and the term K_2b that due electrophoresis and the viscous drag of the solvent.)

Writing $\Lambda_0 = \Lambda + x\sqrt{c}$, we have

$$1 - f_\Lambda = x\sqrt{c}/\Lambda_0 = x\sqrt{2c}/\Lambda_0\sqrt{2},$$

and combining this with equation (3), we obtain

$$b \times 10^8 = (x/\Lambda_0\sqrt{2} - K_1w_1)/K_2 \times 10^{-8}. \quad . \quad . \quad (4$$

Since b is unknown, Debye prefers to put his equation in t form, and to show that the values of b so determined are not inc sistent with our knowledge of their order of magnitude. The diel tric constant of benzonitrile has been taken as 26 at 25°. mobilities of the anion and kation were obtained by the use Kohlrausch's law of the independent migration of ions, and of assumption that the mobility of the tetraethylammonium ion given by the relation (Ulich, *Fortschritte d. Chemie*, 1926, **18**, No. *Trans. Faraday Soc.*, 1927, **23**, 388)

$$\text{mobility} \times \text{viscosity of solvent} = 0{\cdot}295 \quad . \quad . \quad (5$$

For tetraethylammonium iodide Λ_0 was obtained by extrapolat Walden's data (*Z. physikal. Chem.*, 1906, **54**, 189) by the squa root law. Values of the ionic mobilities thus obtained cannot regarded as very trustworthy, but since l_a is approximately eq

to l_c the term $\frac{1}{2}(l_a/l_c + l_c/l_a)$ is not sensitive to changes in l_a and l_c. For silver nitrate, the ionic mobilities were obtained from Koch's measurements of the *E.M.F.* of silver nitrate concentration cells in benzonitrile (this vol., p. 524). The approximate values of the ionic mobilities are: $N(C_2H_5)_4^{\cdot}$ 23·8, I′ 29·5, Br′ 18·4, NO'_3 27·9, Li˙ 17·8, Na˙ 18·6, K˙ 22·6, Ag˙ 24·3.

Inserting numerical values for benzonitrile at 25° in equation (4), we have

$$b \times 10^8 = (x/\sqrt{2}\Lambda_0 - 1{\cdot}439w_1)/0{\cdot}4035 \quad . \quad . \quad . \quad (6)$$

The values of Λ_0 used in calculating b from equation (6) are those obtained by extrapolation by the square-root law. Table VII gives the result of this calculation together with values of b calculated from the respective ionic mobilities on the assumption (1) that the only resistance to the motion of the ions at infinite dilution is the viscous drag of the solvent, and (2) that the magnitude of this drag is given by Stokes's law. This assumption is probably not strictly justified; however, a similar error occurs in equations (3), (4), and (6) since Debye (*Trans. Faraday Soc.*, 1927, **23**, 334) treats the term K_2b as being made up of two parts—one given by Stokes's law, and the other due to the fact that an external force acts on the elements of volume of the liquid (electrophoresis). For comparative purposes this error may therefore be neglected as a first approximation.

TABLE VII.

Values of the Mean Ionic Radius (b) *at* 25° *calculated from Debye and Hückel's Theory.*

Electrolyte.	$b \times 10^8$ (Debye and Huckel), cm.	$b \times 10^8$ (from ionic mobilities at infinite dilution and Stokes's law), cm.
KI	5·16	2·57
NaI	3·72	2·88
LiI	6·47	2·96
LiBr	32·4	3·63
$AgNO_3$	29·9	2·58

The following points may be noted: (1) The values of the mean ionic radii calculated from Debye and Hückel's theory are, except for lithium bromide and silver nitrate, of the correct order of magnitude. They are somewhat larger than in water and methyl alcohol. (2) Frazer and Hartley (*loc. cit.*) found a similar exceptionally large value of b for silver nitrate in methyl alcohol. Were it not for the fact that the value calculated from the ionic mobilities and Stokes's law is not large, one would be tempted to ascribe this large value to solvation and to link it up with the very great solubility of silver nitrate in benzonitrile. (3) For lithium iodide b is larger than for sodium iodide, but potassium iodide occupies an intermediate

position; yet the values of *b* calculated from the ionic mobilities and Stokes's law are in the usual inverse order of atomic weight: $Li^{\cdot} > Na^{\cdot} > K^{\cdot}$.

That only the order of magnitude of *b* and not its exact value is known independently of the theory renders this test much less convincing.

Onsager's Modification of the Debye–Hückel Theory.—Onsager (*Physikal. Z.*, 1926, **27**, 388; 1927, **28**, 277) has recently introduced a refinement into the Debye–Hückel theory by taking into account the Brownian movement of the ions. The final expression at which he arrives does not contain *b*, and does not require a knowledge of the individual ionic mobilities; when the numerical values of universal constants are inserted, it is, for uni-univalent electrolytes,

$$\Lambda = \Lambda_0 - \left[\frac{5{\cdot}78 \times 10^5}{(DT)^{3/2}}\Lambda_0 + \frac{58{\cdot}0}{(DT)^{1/2}\eta}\right]\sqrt{2c} \quad . \quad . \quad (7)$$

For benzonitrile at 25° this becomes

$$\Lambda = \Lambda_0 - (0{\cdot}8475\Lambda_0 + 53{\cdot}14)\sqrt{2c} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The great merit of equations (7) and (8) is that they contain no adjustable constants, and therefore provide a good test for the theory on which they are based. In the following table the slopes of the Λ–$\sqrt{c}$ lines calculated from equation (8) are given under "*x*, calc.," and the observed values under "*x*, obs." The values of Λ_0 used are those calculated by the square-root law, since according to equation (8) the law should hold: the use of values of Λ_0 determined by equation (2) makes very little difference.

Electrolyte.	KI.	NaI.	LiI.	LiBr.	$AgNO_3$.
x, calc.	137·5	132·9	131·9	118·5	137·8
x, obs.	263·3	210·0	283·6	744·5	998·3

For the three iodides the observed slope is about twice as great as the calculated, and for lithium bromide and silver nitrate some 7—8 times. The differences between the observed slopes for the various electrolytes are greater than those between the calculated slopes. It should be mentioned that the agreement of theory with observation is quite good in aqueous and methyl-alcoholic solutions.

Incomplete Dissociation and Applicability of the Law of Mass Action to the Dissociation of Strong Electrolytes.—Bjerrum (*Kgl. Danske Videnskap. Selsk. math.-fys. Medd.*, 1926, VII, 9) suggested that, in concentrated solutions of strong electrolytes, association of ions into electrically neutral doublets occurs. This is the factor which Onsager (*Physikal. Z.*, 1927, **28**, 277) considers accounts for a Λ–$\sqrt{c}$ slope greater than the theoretical. He writes, as an approximation,

$$\Lambda = \Lambda_0 - x\sqrt{c} - \Lambda_0 c/K,$$

where K is the dissociation constant of the electrolyte. However, he states that the mode of ionic association cannot be determined from the conductivity curve, and suggests an investigation of the viscosity and optical properties of the solution. He gives values for the dissociation constants of potassium and thallium nitrates and thallium chloride in water at one concentration only, calculated by comparing the values of Λ for these salts with that of potassium chloride at the same concentration, the last salt being assumed to be completely dissociated.

Fajans (*Trans. Faraday Soc.*, 1927, **23**, 357) has found evidence for the existence of undissociated molecules in concentrated solutions from refractometric data, but the concentrations at which he worked are so great that his results can hardly be said to conflict with the postulates of the Debye–Hückel theory.

Nernst (*Z. Elektrochem.*, 1927, **33**, 428) satisfactorily accounted for the heats of dilution of strong electrolytes in water, one of the most outstanding failures of the Debye–Hückel theory, by assuming incomplete dissociation governed by the law of mass action in addition to the effects due to the Debye–Hückel interionic attraction. He has recently shown (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1928, 4) that, if the greater decrease in equivalent conductivity with increasing concentration of certain electrolytes in water compared with that of potassium iodide and bromide be assumed to be due to incomplete dissociation, values of the degree of dissociation are obtained in approximate agreement with those calculated from the freezing-point depression, the effect of the interionic attraction being taken into account in this latter calculation.

It appears to the author that the law of mass action should be applicable to electrolytic dissociation if there is a sharp distinction between the type of interaction represented by an electrically neutral doublet (undissociated molecule) and that represented by an ion atmosphere of opposite sign surrounding a given ion (the interaction taken account of by the Debye–Hückel theory). The true degree of dissociation (α) is not given by the ratio Λ/Λ_0, since in this expression the decrease in conductivity due to the Coulomb forces between the ions (Debye effect) is not taken into account, and α has, therefore, been evaluated in the following way.

A graph was made of the theoretical relation between Λ and $\sqrt{c}$ deduced from Onsager's expression (8), using values of Λ_0 determined by equation (2). From this graph values of Λ (calculated) at a series of concentrations (c) were read off. The values of Λ (observed) used were those at round concentrations obtained from a plot of Λ against $\log c$. The ratio Λ (obs.)/Λ (calc.), at a given concentration c, gave the first approximation (α_1) to α. From

this value of α_1, the concentration of ions $\alpha_1 c (= c')$ which was responsible for the observed conductivity was calculated. The ratio $\dfrac{\Lambda,\ \text{calculated for an ionic concentration } c}{\Lambda,\ \textit{calculated for an ionic concentration } c'}$ gave the second stage (α_2) in the approximation to α. If the point having the co-ordinates Λ (obs.; total conc. $= c)/\alpha_1\alpha_2$ and $\sqrt{\alpha_2 c'}$ lay within the limits of experimental error on the theoretical Λ–$\sqrt{c}$ straight line, this method of successive approximation was not carried further. The degree of dissociation (α) at concentration c was then given by $\alpha_1\alpha_2$. In very dilute solutions one approximation was sufficient and only very rarely were more than two necessary. Although the *theoretical slope is only slightly altered if values of* Λ_0 *determined* by the square-root law instead of by equation (2) are used, considerably different values of α would be obtained for very dilute solutions, since in this region the differences between the theoretical and observed values are of the same order of magnitude as the differences in the intercepts on the axis of $\Lambda(\Lambda_0)$.

The results of this calculation are given in Table VIII, together with the values of the Ostwald dilution-law constant, $K = \alpha^2/(1-\alpha)v$, calculated from the values of α determined as above. In the cases of silver nitrate and lithium bromide, the theoretical values were calculated from the values of Λ_0 given by the square-root law, since *it was impossible to apply equation (2) to these salts. The error* caused by so doing is not large because the differences between the observed and calculated values of Λ are much greater for these salts than for the iodides of the alkali metals.

Table VIII.

Degree of Dissociation (100α) *of some Strong Electrolytes in Benzonitrile at 25°; and Values of the Ostwald Dilution-law Constant.*

Electrolyte.	Dilution (litres). 20,000	10,000	5,000	2,000	1,000	500	100	
	Degree of dissociation (%).							
*KI	99·72	99·32	98·49	96·24	93·23	—	—	
*NaI	99·77	99·48	98·80	97·27	95·22	91·10	—	
LiI	—	99·24	98·23	95·53	91·40	85·05	70·45	
LiBr	—	82·62	73·73	58·33	43·66	34·50	—	
$AgNO_3$	88·56	82·45	74·46	61·37	50·78	41·14	23·09	
	Ostwald dilution-law constant (1000K).							Mean.
KI	17	14	13	12	13	—	—	13
NaI	21	19	16	17	19	19	—	19
LiI	—	13	11	10	10	10	17	12
LiBr	—	0·39	0·41	0·41	0·34	0·36	—	0·38
$AgNO_3$	0·3	0·4	0·4	0·5	0·5	0·6	0·7	0·5

* $100\alpha = 100$ at $v = 50{,}000$.

When allowance is made for the fact that in extremely dilute solutions α is so nearly 100% that a small error in it results in a relatively large error in $1 - \alpha$, and consequently in K, the constancy of K can be regarded as established.

By the foregoing method we have determined $K = c_{i+}c_{i-}/c$, where c_{i+} and c_{i-} are the concentrations of positive and negative ions and c is that of undissociated molecules. But strictly it is the expression $K' = \gamma_+ c_{i+}\gamma_- c_{i-}/\gamma_\mu c$, where the γ's are the respective activity coefficients, that should hold if the law of mass action applied to the equilibrium between ions and undissociated molecules. Since the activity coefficients involved have not been measured, γ_+ and γ_-, each of which for a uni-univalent electrolyte equals $\gamma_\pm$, have been calculated from the Debye–Hückel theory, and γ_μ has been assumed to be unity at all concentrations. This assumption is not strictly correct, but it is probable that the change in γ_μ with concentration is small compared with that in $\gamma_\pm$, and since γ_μ cannot be calculated, some assumption must be made about it. The equation of Debye and Hückel for the activity coefficient (*Physikal. Z.*, 1923, **24**, 185) is, for a uni-univalent electrolyte,

$$-\log_e \gamma_\pm = \frac{\varepsilon^2}{2DkT}\sqrt{\frac{4\pi\varepsilon^2}{DkT}\Sigma n_i} - \frac{2\pi\varepsilon^4 a}{(DkT)^2}\Sigma n_i \quad . \quad . \quad (9)$$

where k = Boltzmann's gas constant, n_i = the number of ions of the ith kind per c.c. of solution, a = the mean ionic diameter (taken as 6×10^{-8} cm.), and the other symbols are as already defined.

For benzonitrile at 25°, equation (9) becomes

$$-\log_{10}\gamma_\pm = 2{\cdot}66\sqrt{c} - 9{\cdot}12c \quad . \quad . \quad . \quad . \quad (10)$$

Table IX gives the values of the constant $K'(\times 10^3)$.

TABLE IX.

Electrolyte.	Dilution (litres). 20,000	10,000	5,000	2,000	1,000	500	100	Mean.
KI	16	13	11	9	9	—	—	11
NaI	20	17	14	13	14	12	—	14
LiI	—	11	9	8	7	6	8	8
LiBr	—	0·35	0·36	0·33	0·27	0·27	—	0·32
$AgNO_3$	0·31	0·36	0·40	0·40	0·40	0·41	0·41	0·40

The constancy of K' is approximately the same as that of K, and in the case of silver nitrate it is much greater. We may therefore say that the whole of the conductivity–concentration curve can be described by a dissociation governed by the law of mass action, the mobility of the resulting ions varying with their concentration, owing to the Coulomb forces between them, in the manner predicted by the Debye–Hückel–Onsager theory. In extremely dilute solu-

tions dissociation is complete and the change in conductivity with concentration is determined entirely by the Coulomb forces between the ions.

The use of values of Λ_0 obtained from equation (2) in the foregoing calculation is justified since in this way the limiting value of the conductivity at zero concentration is found, no matter how many factors influence the variation of Λ with concentration and without any prejudices as to the nature of these factors, whereas the square-root law can be expected to give a correct result only when the sole factor influencing it is the Coulomb forces between the ions. That this regularity is found by the use of values of Λ_0 determined by equation (2) and not (in some cases) by using those given by the square-root law, indicates that here the deviation of the index n from 0·5 is not due merely to experimental error.

For the sake of comparison the following table is given, which contains values of $\alpha = \Lambda/\Lambda_0$ [Λ_0 being obtained from equation (2)] and the corresponding values of K for sodium iodide at 25°. To apply an activity correction to these values of K is illogical, since if the effect of interionic attraction is neglected in calculating α, it should also be neglected in calculating K. It is seen that K is definitely not constant.

v (litres)	50,000	20,000	10,000	5,000	2,000	1,000	500
100α	98·72	97·84	96·72	94·96	91·34	87·05	80·24
$1000K$	1·5	2·2	2·8	3·6	4·7	5·8	6·5

Summary.

1. The conductivities of the iodides of lithium, sodium, and potassium, of lithium bromide, and of silver nitrate in benzonitrile have been measured over a range of dilution of from $N/500$ to $N/10,000$ or $N/50,000$, and over a range of temperature of from 0° to 70°.

2. The viscosity of benzonitrile over the same range of temperature has been measured.

3. Extrapolation to Λ_0 has been carried out by the square-root law and by Ferguson's method. The merits of the latter method have been discussed.

4. Over almost the whole range of temperature Λ_0 is directly proportional to the fluidity of the solvent.

5. The values of Λ_0 for a given salt have been compared with the values of Λ_0 for the same salt in aqueous, methyl-alcoholic, and nitromethane solution.

6. The slopes of the Λ–$\sqrt{c}$ straight lines are approximately twice as great as those calculated from the Debye–Hückel–Onsager theory.

7. The whole of the conductivity–concentration curve can be

lescribed by a *dissociation governed by the law of mass action*, the nobility of the resulting ions varying with their concentration owing to the Coulomb forces between them, in the manner predicted oy the Debye–Hückel–Onsager theory. In extremely dilute solutions dissociation is complete.

In conclusion, the author wishes to express his warmest thanks to Professor J. C. Philip, F.R.S., for suggesting this subject for research, and for his lively interest in the work. Acknowledgments are also lue to the Department of Scientific and Industrial Research for a naintenance grant and to the Dorset County Council for a Senior County Scholarship.

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LONDON, S.W. 7. [*Received, October 22nd*, 1928.]

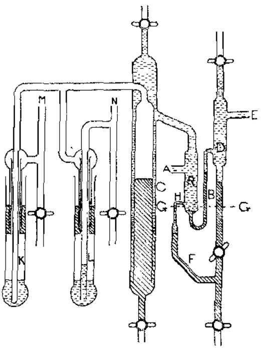
NOTES.

A Gas Circulating Pump. By GUY BARR.

A LARGE number of pumps for the circulation of gas through a closed system have been described in the literature, the intermittent notive power being supplied by an electrical solenoid, a motor, a vacuum pump, etc. The form which is the subject of this note s actuated by water pressure and appears to be capable of many applications in physico-chemical work. An earlier design was nspired by the apparatus described by Maass (*J. Amer. Chem. Soc.*, 1919, **41**, 53), which is operated by a filter-pump; the consumption of water was, however, reduced to little more than the volume of gas moved, by making a direct connexion to the water-main at T and allowing the water to run to waste through tap 2 (Fig. 1, *loc. cit.*). A pump was assembled, on these lines, so as to vary the height of the mercury by some 2 inches only and has been found to be quite satisfactory in operation when a circulation of gas up to about 50 c.c. per minute against a negligible resistance is required. A few simplifications appeared possible and these were incorporated n a second pump which has been constructed to work against heads of several inches of water for some experiments requiring the gas to be circulated through wash-bottles.

At A (see fig.) water from the mains enters a vertical tube, R, at the bottom of which there is an amount of mercury sufficient to fill the narrow tube B when displaced into it. (The bore of B must not be more than about 3·5 mm.) Water flows at the same time into the outer tube of C, which is half full of mercury, and as the pressure rises, this mercury is pushed up the inner tube of C.

The pressure increases until the column of mercury in B is, fairly suddenly, blown out into D; water is then free to escape through B and D to the exit E, so that the pressure in C is released and the "piston" of mercury in the inner tube of C falls. At the beginning of the cycle the U-tube F, connecting R and D, is full of mercury to about the level GG: during the rise of pressure this mercury is of course moved towards D and at the moment of release of pressure the mercury from B is added to the top of the column in D. When the pressure in R and C has fallen sufficiently owing to the escape of water through B, mercury from D siphons over into R through the small tube H at the top of F, and seals B once more. The cycle is then repeated. The figure shows the positions of the mercury levels at a certain stage during the up-stroke of the "piston."

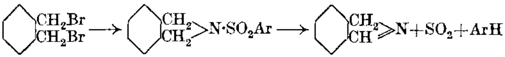


The liquid non-return valves or wash-bottles K, L operate in the usual manner, gas being bubbled through K as the mercury rises in the inner tube of C and sucked through L as it falls. The bottles are detachable for convenience, mercury seals providing a gas-tight connexion with the rest of the apparatus: the washing liquid may therefore be analysed if required. (Alternatively the bottles may be fused on, in which case a tap at the bottom is desirable for addition or removal of the liquid.) Connexion with the apparatus in which gas is to be circulated is made at M and N, the taps below being used for admission and removal of gas. Other stop-cocks are provided for release of air from the water supply, for adjustment of the quantities of mercury in C and F, and for regulation of the rate of fall of the mercury from D during the "blow-off" period. Constriction of the lower end of the inner tube of C would tend to equalise the suction and delivery speeds. The mean position of the mercury in C, and hence the mean pressure in the system beyond M and N, may be varied during an experiment, not only by manipulation of the appropriate taps, but also by adjustment of the position of the discharge end of a piece of rubber tubing attached to E.

The apparatus will circulate up to 100 c.c. of gas per minute against a head of an inch of water, using approximately the same volume of water per minute. Against higher heads the rate of circulation is diminished by wasteful compression in the dead space above the mercury piston. The principle involved may obviously be applied to many other purposes, *e.g.*, to the lifting of mercury in Sprengel or Töpler pumps if sufficient water pressure is available and suitable precautions are taken to prevent the mercury from retaining water.—NATIONAL PHYSICAL LABORATORY. [*Received, October 12th*, 1928.]

An Attempt to Prepare ψ-isoIndole. By GEOFFREY WILLIAM FENTON and CHRISTOPHER KELK INGOLD.

HOLMES and INGOLD having discovered (J., 1926, 1305) that the aromatic sulphonyl derivatives of benzylamine bases, on treatment with concentrated alkalis, yield the corresponding benzylidene-imines, sulphur dioxide, and the appropriate aromatic hydrocarbons, we attempted to exploit this novel reaction for the preparation of *ψ-iso*indole, several more conventional methods of synthesis having already failed to yield this compound. The proposed scheme was as follows :



o-Xylylene dibromide (26·4 g.) was added to a cold suspension of *p*-toluenesulphonamide (17·0 g.) and anhydrous sodium carbonate (10 g.) in a solution of sodium ethoxide (sodium, 4·5 g.) in ethyl alcohol (150 c.c.). The mixture was gently warmed, then boiled for 2 hours, cooled, mixed with water, and nearly neutralised with acetic acid. The precipitated solid contained some unchanged *p*-toluenesulphonamide, which was removed by crystallisation from alcohol; 2-p-*toluenesulphonyldihydro*iso*indole* was then obtained (13 g.) as prisms, m. p. 176° (Found : C, 65·8; H, 5·65. $C_{15}H_{15}O_2NS$ requires C, 65·9; H, 5·5%). The 2-*benzenesulphonyl* derivative, prepared similarly, formed needles, m. p. 140° (Found : C, 64·6; H, 5·3. $C_{14}H_{13}O_2NS$ requires C, 64·9; H, 5·0%).

The *p*-toluenesulphonyl compound, on distillation in an atmosphere of nitrogen with concentrated aqueous potassium hydroxide (*optimum* concentration, 85%; range investigated, 70—near 100%), gave a distillate consisting of toluene and, in small yield, a basic product; and sulphite, but not *p*-cresol, was identified in the alkaline residue, which also contained some tar. The *picrate* of the base separated from alcohol in greenish-yellow leaflets, m. p. 196—197°

(decomp.) after discoloration from about 175°. Analysis indicat that this was the picrate, not of *ψ-iso*indole, but of dihydro*iso*indc (Found: C, 48·8, 48·8, 48·8, 48·6; H, 3·68, 3·69, 3·73, 3·51; 16·12, 16·08. $C_{14}H_{10}O_7N_4$ requires C, 48·5; H, 2·91; N, 16·19 $C_{14}H_{12}O_7N_4$ requires C, 48·3; H, 3·45; N, 16·10%). The benzer sulphonyl derivative, on corresponding treatment, gave a close *similar picrate, m. p. 195—198° (decomp.) with previous discol* ation (Found: C, 48·4, 48·4; H, 3·58, 3·30; N, 16·24, 15·97% Both preparations were extremely similar to, and almost certain identical with, the picrate derived from an authentic sample dihydro*iso*indole prepared as described by v. Braun (*Ber.*, 192 **55**, 2062).

To obtain confirmation of this remarkable result we turned the corresponding 1-methyl homologues, since in this case metho for the production of both the *ψ-iso*indole and its dihydro-derivati have been reported (Gabriel and Neumann, *Ber.*, 1893, **26**, 70 The picrate from 1-methyl-*ψ-iso*indole, prepared as described these authors, decomposed from 135° upwards (Found: C, 50· H, 3·7. Calc.: C, 50·0; H, 3·4%). Our specimen of the picra of the dihydro-derivative had m. p. 151°, and the nitrosoamine h m. p. 100°. By digestion in the cold with an acetone solution *p*-toluenesulphonyl chloride and 10% sodium hydroxide in aqueo acetone, the dihydro-base was quantitatively converted in 2-*p-toluenesulphonyl*-1-*methyldihydro*isoindole, which crystallis from aqueous alcohol in rhombic prisms, m. p. 93° (Found: 66·8, 67·0; H, 6·03, 6·32. $C_{16}H_{17}O_2NS$ requires C, 66·8; H, 5·96%

On distilling this substance in nitrogen with potassium hydroxi (optimum concentration, 75%; range investigated, 70— near 100% toluene, sulphite, a volatile base, and a tar, but no *p*-cresol, we again produced, and in the basic product 1-methyldihydro*iso*indc was definitely identified by the preparation of its nitrosoamine a *p*-toluenesulphonyl derivative.

Hence, although the formation of two of the expected produc (SO_2 and ArH) seems to show that the reaction hoped for mu occur, the third, namely the *ψ-iso*indole, undergoes extensive redu tion during the process. We have not proved that this reducti is complete, and we have not identified the source of the hydroge Our general conclusion is that *ψ-iso*indole must be much less stat than indole, and that this difference is connected with the mo symmetrical distribution of the three elements of unsaturation

the heterocyclic ring of the latter: . This indicates th

he aromatic sextuple valency association is essentially peripheral see Goss and Ingold, this vol., p. 1268).

We wish to thank the Chemical Society for a grant in aid of this nvestigation.—THE UNIVERSITY, LEEDS. [*Received, October 26th,* .928.]

Note on the Paper by Hartley and Barrett on "The Determination of the Density of Liquids." * By JOHN GRINDLEY.

Sir Harold Hartley and W. H. Barrett (J., 1911, **99**, 1072) have nade a careful study of the conditions under which the densities of liquids can be measured with an accuracy of $\pm 0{\cdot}000005$ when relatively small quantities of the liquids are available. The method hey recommend seems entirely suitable for determining the densities of dilute aqueous solutions at temperatures differing little from room emperature, to which attention is specially devoted in their paper, but leads to appreciable errors when the densities of liquids having a larger temperature coefficient of expansion are being determined at temperatures differing by five or more degrees from room temperature. They recommend that the pyknometer be weighed against a counterpoise, equal in volume to that of the full pyknometer, and neglect buoyancy corrections except when the pyknometer is weighed empty. This assumes that the full pyknometer, when in the balance case, has a definite volume, whereas its volume depends first on the coefficient of expansion of the liquid it contains, and secondly on the difference between the temperature at which it was filled, *i.e.*, the temperature at which densities are being determined, and that of the balance case. If the pyknometer be first filled with water and then with some more expansible liquid, both say at 0° or 30°, the volume of the full pyknometer in the balance case *at room temperature, say 15°, will be different in the two cases* and the buoyancy corrections cannot be entirely neglected. It s not essential that the counterpoise be of exactly the same volume as that of the full pyknometer (permissible differences are discussed by Hartley and Barrett), but it is important that the difference between their volumes remains constant throughout a series of experiments. If, for example, a pyknometer of 25 c.c. capacity, whose glass occupies 4 c.c., be filled with water at 0°, its volume at 15° will be 29·018 c.c.; if it be then filled with butyric acid ($d_4^{0°} =$ 0·97844, $d_4^{15°} = 0{\cdot}96344$) at 0°, its volume at 15° will be 29·390 c.c.

* At the request of Sir Harold Hartley, this opportunity is taken of directing attention to a typographical error in the original paper of Hartley and Barrett. Page 1074, line 13 and heading of first column of the table: for (W_1) read $(W_p - W_e)$.

If the volume of the counterpoise be 29·018 c.c., the buoyancy correction is zero when the pyknometer is full of water; when full of butyric acid, its volume is greater than that of the counterpoise by 0·372 c.c., which (at 760 mm. pressure) leads to a buoyancy correction of 0·00048 gram, sufficient to alter the calculated density by 0·000015.

To correct this error, the formula given by Hartley and Barrett must be modified :—

Let V_w and V_l = the volumes of the water and of the liquid, respectively, in the pyknometer at the temperature of the balance case, δ'_w and δ'_l = the densities of water and of the liquid, respectively, at the temperature of the balance case, and let the other symbols used by Hartley and Barrett have the same significance as before; then, instead of their equation (2), read :

(2) $$W_2 = W_p + \delta_w V_p - \Delta_2(V_{pg} + V_w) - (W_c - \Delta_2 V_c),$$

and instead of their equation (3) read :

(3) $$W_3 = W_p + \delta_l V_p - \Delta_3(V_{pg} + V_l) - (W_c - \Delta_3 V_c).$$

Since $\delta_w V_p = \delta'_w V_w$ and $\delta_l V_p = \delta'_l V_l$

and if $V_c = V_{pg} + V_p$,

combination of the above equations (2) and (3) with equation (1) of Hartley and Barrett gives :

$$\delta_l = \delta_w \frac{W_3 - W_1 + \Delta_1(V_c - V_{pg}) + \Delta_3 V_p\left(\frac{\delta_l}{\delta'_l} - 1\right)}{W_2 - W_1 + \Delta_1(V_c - V_{pg}) + \Delta_2 V_p\left(\frac{\delta_w}{\delta'_w} - 1\right)},$$

which approximates closely to the more convenient expression

$$\delta_l = \delta_w \frac{W_3 - W_1 + \Delta_1(V_c - V_{pg}) + \Delta_3 V_p\left(\frac{\delta_l}{\delta'_l} - \frac{\delta_w}{\delta'_w}\right)}{W_2 - W_1 + \Delta_1(V_c - V_{pg})}$$

As can be seen, the added term $\Delta_3 V_p\left(\frac{\delta_l}{\delta'_l} - \frac{\delta_w}{\delta'_w}\right)$ becomes negligible both when densities are determined at temperatures close to room temperature, *i.e.*, $\delta_l/\delta'_l = \delta_w/\delta'_w = 1$, and when the liquid studied has an expansibility similar to that of water, *i.e.*, $\delta_l/\delta'_l = \delta_w/\delta'_w$, in both of which cases the simpler expression of Hartley and Barrett suffices.

The symbol δ_l in the added term can be evaluated with sufficient accuracy by the simpler equation, and δ'_l can be found by interpolation from the densities determined over a range of temperatures.—THE EDWARD DAVIES CHEMICAL LABORATORIES, UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. [*Received, September 5th, 1928.*]

OBITUARY NOTICES.

FREDERICK MOLLWO PERKIN.

BORN NOVEMBER 8TH, 1869; DIED MAY 24TH, 1928.

FREDERICK MOLLWO PERKIN, the son of Sir William Perkin by his second marriage, was born at Sudbury, Middlesex, on November 8th, 1869. He was educated at Amersham Hall School, Reading. On leaving school he studied at the Royal College of Science, at Edinburgh University, and also at the Heriot-Watt College, Edinburgh, and finally at the University of Würzburg, where he took the degree of Ph.D., studying chemistry under Professor Hantzsch.

In 1897 he became head of the Chemical Department of the Borough Polytechnic Institute, a position which he resigned in 1909 in order to enter into practice as a consulting chemist. This work he carried on in the laboratory of his late father, Sir William Perkin, at Sudbury, but he also had a laboratory in London, and in addition for some years he carried on a consulting practice in Bradford.

His first paper, " Some Derivatives of Piperonyl," was published in our Journal (1891, **59**, 150). The work done for his doctorate in Würzburg is to be found in the two joint papers with Hantzsch: " Zur Kentniss der Diazoamidoverbindungen " and " Zur Wanderung von Diazogruppen " (*Ber.*, 1897, **30**, 1394 and 1412). In addition to a number of subsidiary investigations, his chief contributions to chemistry concerned the introduction and elaboration of electrolytic methods for the preparation of organic compounds. Bearing on this, reference may be made to his best-known book, " Practical Methods of Electrochemistry," which was soon recognised as the standard work in English on the subject. The papers describing the results of these investigations were published in part in our Journal, but mainly in the *Transactions* of the Faraday Society.

F. M. Perkin's technical work was concerned largely with the production of fuel oils from coal and from peat, and he was Technical Adviser to the Committee for the Production of Oil from Cannel Coal and Allied Minerals. He worked on the utilisation of peat, and on its conversion into briquettes, on the carbonisation of coal, and the production of smokeless fuels—he may be regarded as one of the pioneers of low-temperature carbonisation.

He took an active part in the foundation of the Faraday Society, was its first Treasurer (1903—1917), and frequently contributed to its *Transactions*. From 1908 to 1916 he was Honorary Secretary to the British Science Guild. He was active in the work of the Paint and Varnish Society, and for a time served as its President, and he was the first President of the Oil and Colour Chemists' Association (1918—1920).

Perkin helped to organise the Chemical Section of the Franco-British Exhibition (1908), and was a member of the juries of that exhibition and of the International Exhibitions held at Brussels (1910), Turin (1911), and Ghent (1913).

For his services to various Government departments during the war he was in 1920 appointed a Commander of the Order of the British Empire.

During the last year of his life his health failed, and he died on May 24th, 1928, in his 59th year.

Perkin married Elizabeth Margaret, daughter of Geo. Mackay of Edinburgh, who with their son and two daughters survives him.

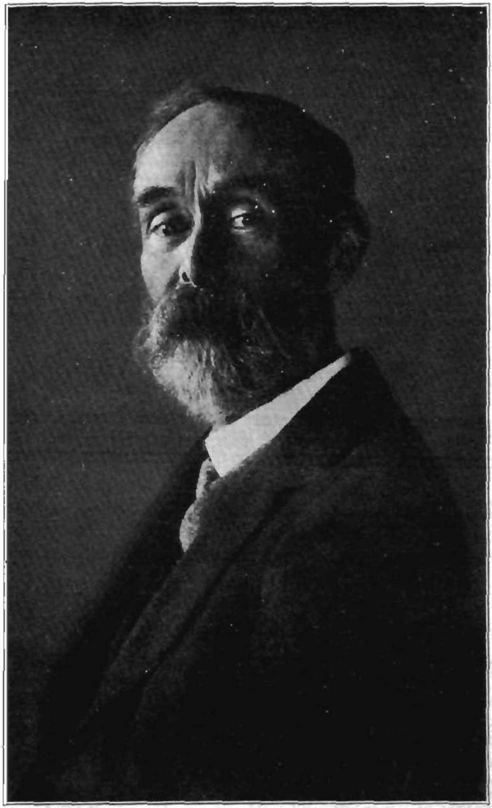
A. J. G.

HENRY RICHARDSON PROCTER.

BORN MAY 6th, 1848; DIED AUGUST 17th, 1927.

AMONG the men of science who have devoted themselves to the improvement of our manufacturing arts, the subject of this notice, Henry Richardson Procter, acclaimed on every side as the pioneer of a scientific leather industry, occupies a conspicuous place of honour. His death has evoked tributes from all parts of the world acknowledging his services to the industry and celebrating his qualities as a scientific investigator, a teacher, and a man rich in qualities of mind and heart.

Henry Richardson Procter was born on May 6th, 1848, at Low-lights, North Shields, his parents both being descendants of the Quaker and tanning family of Richardson. His father maintained the old tannery and designed that Henry, his elder son, should succeed him. At the age of 14 Procter went to Bootham School, York, where, according to an autobiographical note, he had more training in science, for which he already showed an aptitude, than was common in schools of that day. After leaving school he was apprenticed to his father's business and made some efforts to apply his chemical knowledge to tanning, carrying on his scientific studies in an attic laboratory. Having passed the Government "South Kensington" Chemistry Examination, and so become a qualified teacher, he taught a small chemistry class in the town and in con-



H. R. PROCTER.

[To face p. 3300.]

nexion therewith was invited to a week's summer course at the Royal College of Chemistry in Oxford Street, London. There his talents so impressed the authorities that they persuaded him to return to London at Christmas for the rest of the term. At the end of the course he was head of the lists and obtained the full certificate. During part of this time he acted as volunteer assistant to Edward Frankland and Norman Lockyer and so became interested in astronomy. He also published, in conjunction with his relative, T. H. Waller, a translation of Kohlrausch's "An Introduction to Physical Measurements," one of the earliest laboratory books of practical physics to be generally used in this country.

Reluctantly refusing Lockyer's invitation to join the Eclipse expedition, then proceeding to India, Procter returned to his father's tannery and set to work with success in improving and expanding the manufacture. He had little taste for the business side of the industry and as competition within it had become very acute by the time his father died in 1888, he abandoned the paternal tannery and took up the post of chemist to the tanning firm of his relatives, Messrs. S. and J. Richardson, of Elswick, Newcastle-on-Tyne. Here he remained until, in 1890, he was invited by the Yorkshire College, Leeds, to take direction of a new department of applied chemistry which it had been decided to establish for the benefit of the leather industries. The offer, from a worldly point of view, was meagre, but happily the possession of some private means enabled Procter to seize what was to him a tempting opportunity of living in the scientific world and of devoting himself unrestrictedly to scientific work. He took up his post at Leeds early in 1891 and began with very simple accommodation and appliances to devise a course of instruction in the applied science of leather manufacture. In 1898 his department was transferred to a new building provided by the generosity of the Worshipful Company of Skinners of London. These excellent premises were laid out after Procter's design for teaching and research, and they included manufacturing plant on a scale sufficient to afford demonstrations and trials on a valid working scale.

In setting up this new department of applied science, Procter was confronted with the usual difficulty of securing students of adequate preliminary education and intellectual quality. He would have been glad indeed if he could have insisted that students coming to him had previously been equipped fully in fundamental sciences. His own educational and scientific standards were very high, but he was no pedant; he had sympathy with people whose outlook was strongly practical, and his teaching afforded a striking example of the way in which an interest and schooling in scientific

theory and scientific method can be inculcated by an approach from the side of practical problems. It could often be seen how under his guidance and the stimulus of a visible practical end, students previously reluctant would awaken to a perception of the value of chemical theory and apply themselves with zeal to serious scientific study. He produced by his three years course a type of student well trained to address himself to the scientific control and development of the processes of leather manufacture. Students soon came to Procter from all parts of the world and returned to put to effective use the training which they had received.

Before taking up work at Leeds, Procter had gone far towards bringing science to play its due part in the leather industry. His "Text-Book of Tanning," published in 1885, was the first serious effort in the application of science in tannery practice, and is recognised as having inaugurated a scientific era in the industry. It embodies a great deal of original work which he had done since the first publication, in his twenties, of papers on tannin analysis. The difficulty of applying scientific methods to the leather industry came at the outset in the basic substance of the old tannery process—What is tannin and how is the tanning value of a substance to be estimated for the purpose of hoth manufacture and commerce? The first question can only be answered in the vaguest way. There are many tannins, but they present great chemical variety and not much is known about their constitution. They are all derivatives of the aromatic series of carbon compounds, and, so far as is known, all contain either pyrocatechol or pyrogallol, and sometimes phloroglucinol. The pyrogallol tannins yield gallic acid as a decomposition product and many of them glucose. The pyrocatechol tannins contain protocatechuic acid and seem to yield no glucose. The tannins have the one common property of converting skins into leather, and for any scientific control of leather manufacture a standard method of estimating the tanning efficacy, one which will give reproducible results in different hands, is indispensable.

It was to this end that Procter's first efforts were directed, and he devoted great labour to developing the method based on the use of hide powder. During fifty years he returned continually to the subject and he took the principal part as Chairman of the International Commission in drawing up the official method of tannin analysis, published by the International Association of Leather Trades' Chemists in 1907. In the new international method adopted last year, the essential principles of the earlier one are retained.

Apart from his work on tannin analysis, Procter concerned himself with devising simple methods of chemical control for the various

operations of the tan-yard and in his laboratory the biological as well as the chemical aspect of tanning problems was always the subject of study. He took a very active part in the establishment of chrome tanning. He gave to the trade his well-known formula for the making of single-bath chrome liquors and his teaching of the scientific principles of the new methods contributed in a very important way to their adoption and success.

Behind all Procter's active work of the kind just described was the constant occupation of his mind with the fundamental science of colloids. He showed in relation to the newer physical chemistry his remarkable power of bringing himself fully abreast of the times in any special part of theoretical science that he wanted to use, and so equipped he entered upon his *magnum opus*. This was a very complete investigation of the conditions determining the state of equilibrium which is established when gelatin jellies are brought into contact with solutions of acids.* The attainment of equilibrium in such systems is usually associated with swelling or contraction effects which depend on the nature and concentration of the acid solution and are also affected by the presenco of neutral salts.

Procter recognised clearly that such a system is one to which the Donnan theory of membrane equilibria can be applied. In virtue of its basic properties, gelatin combines with acids to form gelatin salts; on ionisation these yield a gelatin kation which is of relatively very large dimensions and consequently unable to pass through membranes which are readily permeable to ionic or molecular entities of smaller size. The interface between a gelatin jelly and its aqueous environment may be regarded as the equivalent of an actual membrane, for the gelatin ions are necessarily confined to the jelly side of the interface, whereas the anions associated with the gelatin kations may pass freely from one side to the other under the influence of osmotic forces, subject, of course, to such restrictions as are attributable to the intervention of electrical forces between the charged ions.

When a gelatin jelly is immersed, for instance, in a solution of hydrochloric acid, the latter passes through the interface, forming the salt gelatin hydrochloride, and ultimately a state of equilibrium is established in which we have gelatin ions, hydrogen ions, and chlorine ions on the jelly side of the interface, whilst hydrogen ions and chlorine ions are in the outer solution. In accordance with Donnan's theory, this equilibrium satisfies the relation

$$[H^+]_1 \cdot [Cl^-]_1 = [H^+]_2 \cdot [Cl^-]_2$$

* The writer has to thank Professor H. M. Dawson for summarising this work. He is also indebted to Mr. J. R. Atkin and Mr. F. C. Thompson of the Leather Industries Department of Leeds University for valuable assistance.

where $[H^+]_1$ and $[Cl^-]_1$ are the concentrations of the hydrogen and chlorine ions in the inner solution and $[H^+]_2$ and $[Cl^-]_2$ are the corresponding quantities for the outer solution. Since both solutions must be electrically neutral, we may also write

$$[G^+] + [H^+]_1 = [Cl^-]_1$$

where $[G^+]$ is the concentration of the gelatin ion. From these relations, it follows as a mathematical consequence that the concentration of the hydrochloric acid when in the jelly must always be less than that in the external solution, and Procter's numerous experiments showed this was actually the case. It follows further that the total ion concentration within the jelly must be greater than that of the external solution. This means that the osmotic pressure within the jelly must be greater than that of the outer solution, and Procter recognised in this inequality the cause of the swelling which, according to his views, proceeds until the difference in the osmotic pressures is counterbalanced by the forces of cohesion in the gel.

This theory, elaborated subsequently in conjunction with J. A. Wilson, has been found to give a satisfactory account of the phenomena associated with the swelling of gelatin. In particular, experiments have shown that there is a close parallelism between the degree of swelling and the difference in the ionic concentrations of the inner and outer solutions in that both pass through a maximum as the acidity of the solution, measured by the p_H value, increases. The maxima occur, in fact, at the same p_H value (compare Atkin, *J. Soc. Leather Trades' Chemists*, 1920, **4**, 248). The theory also affords a simple account of the repression of the swelling which takes place when a salt of the corresponding acid is added to the outer solution.

Procter's work on gelatin thus affords a very notable example of the successful application of the theory of membrane equilibria. The significance of his work from a purely scientific point of view is to be found in the highly satisfactory issue of this attempt to deal with a problem which, even in its essential outlines, had previously been quite obscure. As a result of his investigations, this type of problem was brought within the range of application of modern physico-chemical principles, and in this way he provided a rational basis for the further investigation of colloid systems which is recognised to be of the greatest importance from the purely scientific as well as from the technical point of view. The late Jacques Loeb wrote of Procter's theory of protein swelling as " one of the most ingenious and original contributions to modern science."

Of Procter's contributions to the literature of his subject the "Text-Book of Tanning" has already been mentioned. This was followed in 1898 by the publication of the " Leather Industries

Laboratory Book " and in 1903 by the " Principles of Leather Manufacture." The " Principles " at once took the position which it has retained, that of a standard masterpiece of applied science literature. It has been translated into many languages, including Japanese.

For a full account of Procter's work and the testimony of those who profited from it, the reader is referred to the " Procter Memorial Issue " of the *Journal of the International Society of Leather Trades' Chemists*. Typical of this testimony may be quoted the words of Professor V. Kubelka of Brünn, who, after expressing his own indebtedness, says : " *Je suis certain* qu'il y a *dans* tous les pays du monde des centaines de chemistes de cuir qui se rappelleront avec reconnaissance que pour eux aussi les libres de H. Procter étaient les premiers phares qui les ont conduit dans l'étude de la chimie de cuir." A list of 121 publications gives some idea of the variety of Procter's scientific work and the range of his technical services. Among these services was the foundation in 1897 of the Society just mentioned, which from small beginnings grew to include all the leather chemists of Europe and in other and more remote countries. Procter was its first President and always its central influence.

Procter held his professorship at Leeds until, in 1913, he reached the age of retirement. In anticipation of this event steps had been taken by the leather industry to mark the event by some suitable memorial of the man and his services. The story may perhaps be best expressed in Procter's words : " On my retirement in 1913 a considerable sum, over £1800, was subscribed by my friends as an acknowledgment of what I had done for the chemistry of the trade, and as I have fortunately a modest independent income, I thought that this (the fund) could be most usefully devoted to the *establishment of a special laboratory to investigate the underlying* scientific problems, which, though not likely to be of immediate commercial value, are yet the materials on which sound advance can be based. The money sufficed to erect the laboratory, but unfortunately not to endow it, but it is now open to qualified students of all nations at fees calculated merely to cover their actual cost, and the University, which acts as a Trustee under a Deed-poll, has so far generously borne a good part of the actual working expenses. With more money and more research students, its usefulness might be greatly increased."

Procter's successor, in the person of Dr. E. Stiasny, had already been chosen and had been acting for some time with great success as assistant professor. He now took the vacant Chair and Procter passed into the new Research Laboratory, where with J. A. Wilson

he completed his work on gelatin. The formal opening of the Laboratory by Sir William Ramsay and the attendance of representatives of the industry from all parts of the world was to have taken place in October, 1914. To this plan the outbreak of war put an end. Not only so, but in August Professor Stiasny was in Austria, his native country. In this emergency Professor Procter resumed his old position and busied himself with important work for the War Office, remaining in office till 1918. He was then succeeded by his old pupil, Professor McCandlish, but he continued to work a good deal in his laboratory. In 1923 he sold his house at Ilkley and retired to Newlyn, Cornwall, where, in proximity to his artist son, Ernest, he spent the evening of his life in comfort and content, pursuing old hobbies of handicraft and art and enjoying the society of friends. Towards the end of 1926 he was compelled to take to his bed and he died on August 17, 1927. He was buried at St. Hilary, some miles from Penzance.

Procter had married in 1874 Emma Watson of Newcastle, who died in 1901. He has left a daughter and two sons, the elder, Mr. J. W. Procter, a distinguished architect, the younger the well-known artist, Mr. Ernest Procter.

Procter's success and the sway which he acquired were largely bound up with his remarkable personality. Though he found himself obliged to withdraw from the Society of Friends, he retained in high degree the most admired characteristics of that community. The gentleness of his nature, his single-heartedness and companionableness endeared him to all who knew him and, as Sir Michael Sadler has said most truly, "no Indian guru had disciples more devoted, more respectful." His tastes and talents were of the widest range. In the country he was naturalist, rock-climber, and artist; he was a much travelled man and a good linguist. In leisure hours at home he was a gardener and a craftsman in mechanical and decorative arts and a great reader.

The character of Procter's mind was as markedly philosophical as scientific. The setting up of a "professor of leather" gave scope for a good deal of jest and indeed for some indignation in more austere academic circles. It was a constant delight to his colleagues to witness the effect of Procter's conversation in the University refectory with guests from such circles. He revelled in dialectic and could have excelled any of his colleagues in the arts of casuistry. He exercised a strong quiet influence on University affairs, most of all perhaps by demonstrating in himself and his work the way in which applied science may justify itself among university studies.

The establishment of the unique personal memorial of an inter-

national Research Laboratory and the bestowal of the Fellowship of the Royal Society came towards the end of Procter's life and gave him deep gratification, but he had done his work and given all his discoveries to the industry, seeking neither honours nor rewards.

A. S.

MADYAR GOPAL RAU.

BORN JUNE 17th, 1891; DIED MAY 21ST, 1928.

MADYAR GOPAL RAU, who died of enteric fever at Amritsar on the 21st May, 1928, was born at Mangalore on the 17th June, 1891. His father, Manjunathayya, was a landholder and his mother, Chandravati, was the daughter of a judicial officer in the employ of the East India Company and later of the Madras Government. He received his early education at the Ganapati High School and the Canara High School, matriculating from the latter in 1909 and then entering the Government College, Mangalore (University of Madras). After passing the Intermediate Examination in 1911, he left Mangalore for the Presidency College, Madras. Here his ability was early recognised and he qualified for the B.A. degree in 1913, being at the top of the class list. Two years later he took an Honours degree in chemistry, being once more at the head of the list. He was awarded a University Research Studentship and for the following three years he worked at research in organic chemistry under the direction of the writer. During part of this period he was called upon to take complete charge of the teaching of organic chemistry at the Presidency College and he thus had an early opportunity of showing his aptitude for teaching. He was in 1918 appointed a lecturer in the College. In 1920 he moved to the Forest Research Institute and College, Dehra Dun, as Assistant to the Forest Chemist and he remained there until, in 1925, he was appointed Professor of Chemistry at the Khalsa College, Amritsar. He held this post at the time of his death and in addition he had for the last year been Principal of the College.

Nearly all Gopal Rau's research work had been carried out in collaboration with the writer. His early work was concerned with the nitration and bromination of acetamidomethoxybenzoic acids (J., 1917, **111**, 70, 221; 1918, **113**, 22, 783) and with an attempt to synthesise morindone (J., 1921, **119**, 1339), but after proceeding to Dehra Dun he worked mainly on natural products. He published a number of papers on essential oils and fats which appeared in the Journal and in the Indian Forest Records (J., 1922, **121**, 876; 1923, **123**, 550; *Ind. For. Rec.*, 1922; **9**, 95, 111; 1925, **11**, 197, 207; *J. Ind. Inst. Sci.*, 1926, **9**, *A*, 111). His most important work

was on the oxidation of Δ^3-carene, the constituents of the essential oil from *Blumea Malcomii*, and on the effect of anti-catalysts on the rate of oxidation of some dicyclic terpenes. He also collaborated in two papers on the constitution of abietic acid. After his appointment to Amritsar he had little time for original work, as he was much occupied with teaching and administrative duties and the facilities for laboratory work were not good. Although he never ceased to work in the laboratory, he only published one paper on "The essential oil from the flower-heads of *Perovskia atriplicifolia*, Benth." (*J. Ind. Chem. Soc.*, 1926, **3**, 141). He felt very keenly his lack of opportunity for work and he had arranged to visit England in September in order to work with Prof. Robinson at University College, but this was not to be. Though physically never very strong, he was a keen cricketer and tennis player and by his premature death at the age of 37 India loses an organic chemist of a type all too rare in that country, a loss which she can ill afford. Although not possessing great originality, Gopal Rau was a fine experimentalist and an inspiring teacher. In May, 1912, he married Miss Giriji Bai of Honavar (Bombay), who survives him.

J. L. Simonsen.

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FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arrar according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 gr C_2 group, etc.).

Secondly, according to the number of other elements besides carbon containe the molecule (thus 5 IV indicates that the molecule contains five carbon atoms four other elements).

Thirdly, according to the nature of the elements present in the molecule (give the above order).

Fourthly, according to the number of atoms of each single element (except car present in the molecule.

Salts are placed with the compounds from which they are derived. The chlori bromides, iodides, and cyanides of quaternary ammonium bases, however, are regist as group-substances.

C_1 Group.

CO Carbon monoxide, decomposition of, in the corona discharge (OTT), 1: inflammation of mixtures of air and (MAXWELL and WHEELER), 15; effe catalysts on flame speed, infra-red emission, and ionisation during combustio oxygen and (GARNER and JOHNSON), 280.

CS_2 Carbon disulphide, ignition of (WHITE), 751.

1 II

CHN Hydrocyanic acid, and its alleged isomerides (COATES, HINKEL, and ANG 540; cuprous salt, action of methyl iodide on (HARTLEY), 780.

CH_2N_2 Diazomethane, acylation of (BRADLEY and SCHWARZENBACH), 2904; ac of benzoyl chloride with (BRADLEY and ROBINSON), 1310.

CH_2S_3 Trithiocarbonic acid (MILLS and ROBINSON), 2330.

CH_2S_2 Tetrathiocarbonic acid, and its ammonium salt (MILLS and ROBINS 2330.

CH_3I Methyl iodide, action of cuprous cyanide on (HARTLEY), 780.

CH_5N Methylamine, action of nitrous acid on (TAYLOR), 1100.

CH_5N_3 Guanidine, and its carbonate, hydrolysis of (BELL), 2074.

1 III

CH_6ON_4 *Carbohydrazide, reactions of (MUNRO and WILSON), 1257.*

C_2 Group.

C_2H_2 Acetylene, action of sulphur on, up to 650° (PEEL and ROBINSON), 2068.

2 II

$C_2H_2O_2$ Glyoxal, photochemical decomposition of (NORRISH and GRIFFITI 2829.

$C_2H_2O_4$ Oxalic acid, complex molybdenum salts of (SPITTLE and WARDLA 2742.

$C_2H_4O_2$ Acetic acid, inert salt effects in catalysis by, and its salts (DAWSON and KEY), 1248; lead subsalt, and its reactions with phenols (GIBSON and MATTHEWS), 596; magnesium salt, constitution of solutions of (GOODE, BAYLISS, and RIVETT), 1950.

$C_2H_8N_2$ Ethylenediamine, equilibria of phenols with (PUSHIN and SLADOVICH), 837.

2 III

C_2HOCl_3 Chloral, action of, on phenylhydrazines (CHATTAWAY and DALDY), 2756; condensations of, with anisic acid, *p*-nitroanisole, and 2:6-dichloroquinol (CHATTAWAY and CALVET), 2913; condensation of, with substituted phenols (CHATTAWAY and CALVET), 1088.

$C_2H_2OCl_2$ Dichloroacetaldehyde, condensation of phenols with (CHATTAWAY and MORRIS), 3241.

C_2H_3OCl *Acetyl chloride, speed of bromination of* (WATSON), 1137.

C_2H_3OBr Acetyl bromide, speed of bromination of (WATSON), 1137.

C_2H_3Ng Mercuric methyl cyanide (COATES, HINKEL, and ANGEL), 542.

$C_2H_4O_4N_2$ *β*-Hydroxyethylnitrolic acid (EARL, ELLESWORTH, JONES, and KENNER), 2701.

$C_2H_7O_4As$ *β*-Hydroxyethylarsinic acid, and its calcium salt (GOUGH and KING), 2432.

2 IV

$C_2H_2O_2ClBr$ Chlorobromoacetic acid, racemic, resolution of (BACKER and MOOK), 2125.

$C_2H_6O_3ClAs$ *β*-Chloroethylarsinic acid (GOUGH and KING), 2434.

C_3 Group.

$C_3H_4O_4$ Malonic acid, condensation of *cyclo*hexanealdehyde and (SIRCAR), 54.

C_3H_6O Acetone, water catenary in iodination of (*DAWSON and KEY*), 543.

C_3H_9N Trimethylamine, velocity of reaction of, with nitrobenzyl chlorides (NORRISH and SMITH), 130.

$C_3H_{11}N_3$ Triaminopropane, complex palladium and platinum salts of (MANN), 890.

3 III

C_3H_5OCl Chloroacetophenone, formation of, from benzoyl chloride (BRADLEY and SCHWARZENBACH), 2904.

$C_3H_6O_2N$ *d*-Glutamic acid, action of aniline on (GRAY), 1264.

$C_3H_6N_2S$ Ethylenethiocarbamide, complex metallic salts with (MORGAN and BARTLETT), 143.

$C_3H_6Cl_3As$ *γ-Chloropropyldichloroarsine* (*GOUGH and KING*), 2439.

$C_3H_7O_3N$ *β*-Nitropropanol, sodium salt (EARL, ELLESWORTH, JONES, and KENNER), 2702.

$C_3H_9O_3B$ Methyl borate, preparation and constants of (ETRIDGE and SUGDEN), 991.

$C_3H_9O_4As$ *γ*-Hydroxypropylarsinic acid, and its calcium salt (GOUGH and KING), 2439.

3 IV

$C_3H_6ON_4S$ 3-Amino-2:4-diketotetrahydrothiazole 2-hydrazone (STEPHEN and WILSON), 1418.

$C_3H_7O_4SLi$ Acetone lithium hydrogen sulphate (FRIEND and POUNDER), 2248.

$C_3H_8O_3ClAs$ *γ*-Chloropropylarsinic acid, and its salts (GOUGH and KING), 2440.

$C_3H_{10}O_3NAs$ *γ*-Aminopropylarsinic acid (GOUGH and KING), 2440.

$C_3H_{11}N_3Cl_2Pt$ Chlorotriaminopropaneplatinous chloride (MANN), 896.

$C_3H_{12}N_3Cl_3Pt$ Dichloro(triaminopropane-hydrochloride) platinum (Mann), 895.

$C_3H_{12}N_3Cl_3Pd$ Dichloro(triaminopropane-γ-hydrochloride) palladium (Mann), 897.

3 V

$C_3H_2O_2N_3S_3Mo$ Dihydrogen molybdenum dioxytrithiocyanate, and its salts (James and Wardlaw), 2732.

C_4 Group.

$C_4H_4O_6$ Tartaric acid, triethylenediaminenickel salt (Bucknall and Wardlaw), 2741.

C_4H_4S Thiophen, production of, from acetylene and carbon disulphide (Briscoe, Peel, and Robinson), 2657.

C_4H_4Se Selenophen (Briscoe and Peel), 1741; (Briscoe, Peel, and Robinson), 2628.

$C_4H_6O_3$ *Acetic* anhydride, *physical properties of* (Jones), 1193; *miscibility of* (Jones and Betts), 1177; action of bromine on (Watson and Roberts), 2779.

$C_4H_6O_4$ Acetyl peroxide, decomposition of (Walker), 2040.

$C_4H_6O_5$ Malic acid, optical activity of, in presence of sodium molybdate (Patterson and Buchanan), 3006.

$C_4H_6Br_2$ Butadiene dibromides, isomeric (Farmer, Lawrence, and Thorpe), 729.

$C_4H_8O_2$ Ethyl acetate, catalysis by hydrochloric acid of hydrolysis of (Dawson and Lowson), 2146.

$C_4H_{10}O$ Ethyl ether, action of disilicon hexachloride on (Kipping and Thompson), 1989.

$C_4H_{12}N_2$ β-Methyltrimethylenediamine, complex platinum salts of (Mann), 1261.

C_4Cl_4Se Tetrachloroselenophen (Briscoe and Peel), 1747.

C_4Br_4Se Tetrabromoselenophen (Briscoe and Peel), 1746.

4 III

$C_4H_4ON_2$ Glyoxaline-4(5)-formaldehyde, and its salts (Hubball and Pyman), 21.

$C_4H_4Cl_4S$ αββ'-Tetrachlorodiethyl sulphide (Mumford and Phillips), 160.

$C_4H_4Cl_6S$ ααββββ'-Hexachlorodiethyl sulphide (Mumford and Phillips), 160.

$C_4H_5ON_3$ Glyoxaline-4(5)-formaldoxime (Hubball and Pyman), 25.

$C_4H_5Cl_3S$ αββ'-Trichlorodiethyl sulphide (Mumford and Phillips), 160.

$C_4H_6O_2S_2$ 1:3-Dithiolan-2-carboxylic acid (Chivers and Smiles), 700.

C_4H_7ON Acetonecyanohydrin, preparation of (Welch and Clemo), 2629.

$C_4H_8O_2S_2$ Dithian monoxide, and its salts (Bell and Bennett), 90.

$C_4H_8O_2S_2$ Dithian dioxides, and their salts (Bell and Bennett), 88.

$C_4H_8Cl_2S$ ββ'-Dichlorodiethyl sulphide, chlorination of (Mumford and Phillips), 155.

$C_4H_{10}O_2Cu$ Cupric ethoxide (Doak and Packer), 2768.

$C_4H_{10}O_2Te$ *Diethyltellurone* (Gilbert and Lowry), 3182.

$C_4H_{10}Cl_2Te$ Diethyltelluronium dichlorides (Gilbert and Lowry), 3183.

$C_4H_{10}Br_2Te$ Diethyltelluronium dibromides (Gilbert and Lowry), 3183.

$C_4H_{10}I_2Te$ Diethyltelluronium di-iodides (Gilbert and Lowry), 3185.

$C_4H_{10}I_4Te$ α-Diethyltelluronium α-tetraiodide (Gilbert and Lowry), 3181.

4 IV

$C_4H_6O_2N_4S$ *2:4-Diketotetrahydrothiazole 2-semicarbazone* (Stephen and Wilson), 1421.

$_4H_6O_2Br_2S_2$ 1:3-Dithiolan-2-carboxylic acid dibromide (CHIVERS and SMILES), 700.

$_4H_6O_2I_2S_2$ 1:3-Dithiolan-2-carboxylic acid di-iodide (CHIVERS and SMILES), 700.

$_4H_6ON_4S$ 3-Amino-2:4-diketo-5-methyltetrahydrothiazole 2-hydrazone (STEPHEN and WILSON), 1418.

$_4H_{12}O_3NAs$ β-Dimethylaminoethylarsinic acid, and its hydrochloride (GOUGH and KING), 2435.

4 V

$_4H_{12}ONCl_4Mo$ Tetramethylammonium molybdenyl tetrachloride (JAMES and WARDLAW), 2738.

C_5 Group.

$_5H_8$ Isoprene, hydrogenation of (LEBEDEV and YAKUBCHIK), 828.

5 II

$_5H_5N$ *Pyridine, nuclear fission of* (SHAW and WILKIE), 1377; inhibition of esterification by (BAILEY), 1204; additive compound of phosphoryl chloride and (BOYD and LADHAMS), 218.

$_5H_8O_2$ β-Methylbutyrolactone, and its silver salt (SIRCAR), 901.

$_5H_{10}O$ Dimethyltrimethylene oxides (BENNETT and PHILIP), 1938.

$_5H_{10}O_5$ Lyxose, structure of (HIRST and SMITH), 3147.

$_5H_{10}Te$ *cyclo*Telluropentane (MORGAN and BURGESS), 327.

$_5H_{11}N$ Piperidine, interaction of, with derivatives of xanthone and diphenylene oxide (LE FÈVRE), 3249.

$_5H_{12}O$ Methyl *sec.*-butyl ether (BENNETT and PHILIP), 1931.

5 III

$_5H_6ON_2$ Methylglyoxalineformaldehydes, salts of (HUBBALL and PYMAN), 27, 28.

$_5H_6O_2N_2$ 5-Carboxy-1-methylglyoxaline, picrate of (HUBBALL and PYMAN), 28.

$_5H_7ON_5$ Glyoxaline-4(5)-formaldehyde semicarbazone (HUBBALL and PYMAN), 25.

$_5H_7O_2Mo$ Molybdenyl acetylacetone (MORGAN and CASTELL), 3255.

$_5H_8ON_2$ 1-Methyl-5-hydroxymethylglyoxaline, picrate of (HUBBALL and PYMAN), 28.

$_5H_8O_2S_2$ 1:3-Dithian-2-carboxylic acid (CHIVERS and SMILES), 701.

$_5H_{10}O_2Te$ *cyclo*Telluripentane 1:1-dioxide (MORGAN and BURGESS), 327.

$_5H_{10}Cl_2Te$ *cyclo*Telluripentane 1:1-dichloride (MORGAN and BURGESS), 325.

$_5H_{10}Br_2Te$ *cyclo*Telluripentane 1:1-dibromide (MORGAN and BURGESS), 326.

$_5H_{10}I_2Te$ *cyclo*Telluripentane 1:1-di-iodide (MORGAN and BURGESS), 328.

$_5H_{13}ON$ γ-Amino-β-hydroxy-β-methylbutane, and its salts (READ and REID), 1491.

5 IV

$_5H_8O_2S_2I_2$ Di-iodo-1:3-dithian-2-carboxylic acid (CHIVERS and SMILES), 701.

$_5H_{10}ONCl$ α-Chloro-γ-imino-γ-ethoxypropane, hydrochloride of (CLEMO and WATSON), 729.

$_5H_{10}ON_4S$ 3-Amino-2:4-diketo-5-ethyltetrahydrothiazole 2-hydrazone (STEPHEN and WILSON), 1419.

$_5H_{14}O_3NAs$ γ-Dimethylaminopropylarsinic acid, and its hydrochloride (GOUGH and KING), 2441.

$_5H_{15}O_6NAs_2$ Methyldiethylamine-ββ′-diarsinic acid (GOUGH and KING), 2435.

5 V

$C_5H_3ON_5S_5Mo$ Dihydrogen molybdenyl pentathiocyanate, salts of (JAMES and WARDLAW), 2736.

$C_5H_{15}O_3NClAs$ *β-Dimethylaminoethylarsinic acid methochloride* (GOUGH and KING), 2435.

C_6 Group.

C_6H_6 Benzene, velocity measurements in relation to substitution in (BRADFIELD and JONES), 3073.

C_6H_{14} *n*-Hexane, oxidation of (BRUNNER and RIDEAL), 1162, 2824.

6 II

C_6H_7N Aniline, action of *d*-glutamic acid with (GRAY), 1264.

$C_6H_8O_6$ Propane-αα γ-tricarboxylic acid (LENNOX and PERKIN), 1524.

$C_6H_{10}O$ Mesityl oxide, catalysis in iodination of (DAWSON and KEY), 2154.

$C_6H_{10}O_2$ *β-Ethylbutyrolactone, and its silver salt* (SIRCAR), 901.

β-Methylvalerolactone, and its silver salt (SIRCAR), 902.

$C_6H_{10}O_3$ Ethyl acetoacetate, condensations with (FRANKLIN and SHORT), 591; condensation of ketones with (JUPP, KON, and LOCKTON), 1638; reactions of with distyryl ketones (HEILBRON and HILL), 2863.

$C_6H_{12}O_3$ *n*-Butoxyacetic acid (RULE, HAY, and PAUL), 1356.

$C_6H_{12}O_6$ Galactose, mutarotation of (SMITH and LOWRY), 666

6 III

$C_6H_2O_{10}N_6$ Pentanitroaniline (FLÜRSCHEIM and HOLMES), 3041.

$C_6H_3O_3Cl_9$ Parachlorals (CHATTAWAY and KELLETT), 2711.

$C_6H_3N_6Fe$ *Hydroferricyanic acid, potassium salt, solubility of, in water* (FRIEND and SMIRLES), 2242.

$C_6H_4O_2Cl_2$ 2:6-Dichloroquinol, condensation of chloral with (CHATTAWAY and CALVET), 2913.

$C_6H_4O_8N_4$ 2:4:6-Trinitro-5-aminoresorcinol (FLÜRSCHEIM and HOLMES), 3044.

C_6H_4ClF *p*-Fluorochlorobenzene, nitration of (INGOLD and VASS), 2265.

C_6H_5BrMg Magnesium phenyl bromide, action of, on methyl *o*-cyanobenzoate (BOYD and LADHAMS), 2089.

$C_6H_6O_6N_6$ 2:4:6-Trinitro-1:3:5-triaminobenzene (FLÜRSCHEIM and HOLMES) 3045.

$C_6H_8ON_2$ 1:4-Dimethylglyoxaline-5-formaldehyde, and its picrate (HUBBALL and PYMAN), 29.

$C_6H_8O_2N_2$ *1:4-Dimethylglyoxaline-5-carboxylic acid, and its picrate* (HUBBALL and PYMAN), 30.

Methyl 1-methylglyoxalinecarboxylates (HUBBALL and PYMAN), 31.

$C_6H_8O_6Tl_6$ Thallium sorbitol (MENZIES and KIESER), 190.

$C_6H_9O_5Tl_3$ Trithallium methylarabinoside (MENZIES and KIESER), 188.

$C_6H_{11}ON$ *Methylpentenoic amides* (GOLDBERG and LINSTEAD), 2355.

$C_6H_{11}O_7Tl$ Thallous gluconate (MENZIES and KIESER), 189.

$C_6H_{14}NCl$ β-Chloroethyldiethylamine, and its salts (GOUGH and KING), 2436.

$C_6H_{15}O_3B$ Ethyl borate, preparation and constants of (ETRIDGE and SUGDEN) 992.

$C_6H_{15}ITe$ *Triethyltelluronium iodide* (GILBERT and LOWRY), 3184.

6 IV

$C_6H_2O_7N_3F$ 3-Fluoro-2:4:6-trinitrophenol (HODGSON and NIXON), 1882.

$C_6H_3O_5N_2F$ Fluorodinitrophenols, and their salts (HODGSON and NIXON), 1881.

$C_6H_4O_3NF$ Fluoronitrophenols, and their salts (HODGSON and NIXON), 1880.

$C_6H_5ONCl_2$ 2:4-Dichloro-6-aminophenol, hydrochloride of (HUNTER and BARNES), 2056.

$C_6H_5ONI_2$ 2:4-Di-iodo-6-aminophenol, hydrochloride of (HUNTER and BARNES), 2058.

$C_6H_5O_2ClS$ Chlorobenzene-*p*-sulphinic acid, and its ammonium salt (DAVIES and WOOD), 1126.

$C_6H_5O_6ClS_2$ Chlorobenzene-2:4-disulphonic acid, and its potassium salt (DAVIES and WOOD), 1124.

$C_6H_5O_9ClS_3$ Chlorobenzene-2:4:6-trisulphonic acid, and its potassium salt (DAVIES and WOOD), 1125.

C_6H_5NClF 3-Fluoro-4-chloroaniline (INGOLD and VASS), 422.

C_6H_5NBrI 2-Bromo-4-iodoaniline (BRADFIELD, ORTON, and ROBERTS), 783.

C_6H_6ONCl *Chloroaminophenols, and their hydrochlorides* (HODGSON and KERSHAW), 2704.

C_6H_6ONBr Bromoaminophenols, and their hydrochlorides (HODGSON and KERSHAW), 2704.

C_6H_6ONI *p*-Iodo-*o*-aminophenol, hydrochloride of (HUNTER and BARNES), 2057.
Iodoaminophenols, and their hydrochlorides (HODGSON and KERSHAW), 2704.

$C_6H_6O_4NAs$ 5-Amino-2-hydroxyphenylarsenoxide, salts of (NEWBERY and PHILLIPS), 2379.

$C_6H_6O_2N_3Cl$ Chloronitrophenylhydrazines (PLANT and ROSSER), 2461.

$C_6H_6O_6NAs$ 4-Nitro-3-hydroxyphenylarsinic acid, and its salts (BALABAN), 810.

$C_6H_7O_4NS$ 6-Amino-2:4-bistrichloromethyl-1:3-benzdioxin (CHATTAWAY and COULSON), 1090.

$C_6H_7O_6N_2As$ 2-Nitro-4-amino-3-hydroxyphenylarsinic acid, and its magnesium salt (BALABAN), 811.
5-Nitro-4-amino-3-hydroxyphenylarsinic acid (BALABAN), 3071.

$C_6H_{15}NCl_2As$ γ-*n*-Propylaminopropyldichloroarsine hydrochloride (GOUGH and KING), 2442.

$C_6H_{16}O_2NAs$ γ-*n*-Propylaminopropylarsinic acid, and its hydrochloride (GOUGH and KING), 2441.

$C_6H_{18}O_9NAs_3$ Triethylamine-ββ′β″-triarsinic acid, and its salts (GOUGH and KING), 2434.

$C_6H_{22}N_6Br_2Pt$ Bis(triaminopropane)platinous dibromide (MANN), 897.

$C_6H_{22}N_6I_2Pt$ Bis(triaminopropane)platinous di-iodide (MANN), 897.

$C_6H_{24}N_6Cl_2Ni$ Triethylenediaminenickel chloride (BUCKNALL and WARDLAW), 2741.

6 V

$C_6H_2O_4N_2BrI$ 1-Bromo-3-iodo-4:6-dinitrobenzene (MAYES and TURNER), 693.

$C_6H_3O_2NClF$ *Fluorochloronitrobenzenes* (INGOLD and VASS), 422.

$C_6H_3O_2NBrI$ 1-Bromo-3-iodo-6-nitrobenzene (MAYES and TURNER), 693.

$C_6H_4O_2N_2ClI$ Chloroiodo-6-nitroanilines (BRADFIELD, ORTON, and ROBERTS), 784.

$C_6H_4O_2N_2BrI$ Bromoiodo-6-nitroanilines (BRADFIELD, ORTON, and ROBERTS), 784.

$C_6H_4O_5NClS$ 1-Chloro-2-nitrobenzene-4-sulphonic acid, and its potassium salt (DAVIES and WOOD), 1125.

$C_6H_4NClBrI$ Chlorobromoiodoanilines (BRADFIELD, ORTON, and ROBERTS), 783.

$C_6H_5ONClBr$ Chlorobromoaminophenols, and their hydrochlorides (HUNTER and BARNES), 2060.

C_6H_5ONClI Chloro-6-iodoaminophenols, and their hydrochlorides (HUNTER and BARNES), 2061, 2065.

C_6H_5ONBrI Bromoiodoaminophenols, and their hydrochlorides (HUNTER and BARNES), 2062.

$C_6H_5O_3N_2I_2As$ 3-Nitro-4-hydroxy-5-aminophenyldi-iodoarsine, hydriodide of (NEWBERY and PHILLIPS), 2381.

$C_6H_5O_4NClAs$ 3-Chloronitrophenylarsinic acids, and their salts (BALABAN), 810.

$C_6H_6ONCl_2As$ 5-Amino-2-hydroxyphenyldichloroarsine, hydrochloride of (NEWBERY and PHILLIPS), 2379.

$C_6H_6ONI_2As$ Aminohydroxyphenyldi-iodoarsines, hydriodides of (NEWBERY and PHILLIPS), 2378.

$C_6H_7ON_2Cl_2As$ 3:5-Diamino-4-hydroxyphenyldichloroarsine, hydrochloride of (NEWBERY and PHILLIPS), 2377.

$C_6H_7O_2N_2I_2As$ 3:5-Diamino-4-hydroxyphenyldi-iodoarsine, hydriodide of (NEWBERY and PHILLIPS), 2378.

$C_6H_7O_4N_2ClS_2$ Chlorobenzene-2:4-disulphonamide (DAVIES and WOOD), 1125.

$C_6H_{12}ON_4S_2As_2$ Ethylenethiocarbamido-argentous oxide, and its salts (MORGAN and BURSTALL), 151.

$C_6H_{12}ON_4S_2Au_2$ Ethylenethiocarbamido-aurous oxide, and its salts (MORGAN and BURSTALL), 153.

$C_6H_{12}ON_4S_2Cu_2$ Ethylenethiocarbamido-cuprous oxide and its salts (MORGAN and BURSTALL), 149.

$C_6H_{17}O_3NClAs$ γ-Dimethylaminopropylarsinic acid methochloride (GOUGH and KING), 2441.

$C_6H_{18}O_6NClAs_2$ Dimethyldiethylammonium chloride ββ′-diarsinic acid (GOUGH and KING), 2435.

$C_6H_{20}ON_2Cl_5Mo$ Ditrimethylammonium molybdenyl pentachloride (JAMES and WARDLAW), 2737.

C_7 Group.

C_7H_5N Benzonitrile, electrical conductivity of uni-univalent salts in (MARTIN), 3270.

C_7H_7F Benzyl fluoride, preparation and properties of (C. K. and E. H. INGOLD), 2249.

C_7H_8O *m*-Cresol, influence of electrolytes on solubility of, in water (CARTER and HARDY), 127.

$C_7H_8O_3$ 5-Methyl*dicyclo*pentan-3-one-1-carboxylic acid (GOSS and INGOLD), 1273.

$C_7H_{12}O$ *cyclo*Hexanealdehyde, condensation of malonic acid and (SIRCAR), 54.
Suberone, preparation of (VOGEL), 2032.

$C_7H_{12}O_2$ β-Ethylvalerolactone, and its silver salt (SIRCAR), 902.
β-Methyl-β-ethylbutyrolactone, and its silver salt (SIRCAR), 901.

$C_7H_{12}O_4$ Ethyl malonate, sodium salt, action of dibromotetracarboxylic esters on (LENNON and PERKIN), 1513.
l-*iso*Propylsuccinic acid, and its salts (HENRY and PAGET), 78.

$C_7H_{12}O_5$ Dimethyl γ-xylonolactone (HAWORTH and PORTER), 616.

$C_7H_{14}O_3$ *n*-Amyloxyacetic acid (RULE, HAY, and PAUL), 1356.

7 III

$C_7H_4O_2Br_2$ Dibromohydroxybenzaldehydes (HODGSON and JENKINSON), 2275.

$C_7H_4O_6N_2$ 3:5-Dinitrosalicylaldehyde (LOVETT and ROBERTS), 1978.

C_7H_5OCl Benzoyl chloride, action of diazomethane with (BRADLEY and ROBINSON), 1310.

C_7H_6ClI 3-Chloro-5-iodotoluene (MCALISTER and KENNER), 1915.

C_7H_6BrI 3-Bromo-5-iodotoluene (MCALISTER and KENNER), 1914.

$C_7H_7ON_3$ 1-Methoxy-1:2:3-benztriazole (BRADY and REYNOLDS), 198.
1-Methyl-1:2:3-benztriazole 1-oxide (BRADY and REYNOLDS), 198.

$C_7H_7O_2N$ Phenylnitromethane, constitution and substitution of (FLÜRSCHEIM and HOLMES), 453.

$C_7H_7O_3N$ *p*-Nitroanisole, condensation of chloral with (CHATTAWAY and CALVET), 2913.

C_7H_7ON Benzaldoxime, nitration of (BRADY and MILLER), 337.

$C_7H_8O_3S$ Toluene-*p*-sulphonic acid, ammonium salt (CLEMO and WATSON), 726.

$C_7H_8Br_2Se$ Phenyl methyl selenide dibromide (EDWARDS, GAYTHWAITE, KENYON, and PHILLIPS), 2300.

$C_7H_8I_2Se$ Phenyl methyl selenide di-iodide (EDWARDS, GAYTHWAITE, KENYON, and PHILLIPS), 2300.

$C_7H_9O_3N$ 5 Methyl*dicyclo*pentan-3-one-1-carboxylic acid oxime (GOSS and INGOLD), 1273.

$C_7H_9O_3Sb$ *p*-Tolylstibinic acid (GODDARD and YARSLEY), 721.

$C_7H_{10}N_2S$ Methylthiolphenylhydrazines (HODGSON and HANDLEY), 1884.

$C_7H_{13}O_2Tl$ *Thallium dimethyl acetylacetone* (MENZIES, SIDGWICK, CUTCLIFFE, and FOX), 1289.

$C_7H_{14}O_3N_4$ Ethyl acetoacetate δ-aminosemicarbazone (MUNRO and WILSON), 1260.

$C_7H_{16}O_4S_2$ Sulphonal, parachor for (FREIMAN and SUGDEN), 268.

$C_7H_{17}NCl_2$ Methyl-β-chloroethyldiethylammonium chloride (GOUGH and KING), 2437.

7 IV

$C_7H_3O_4NBr_2$ Dibromonitrohydroxybenzaldehydes (HODGSON and JENKINSON), 2278.

$C_7H_3O_6N_2Cl$ Chlorodinitrohydroxybenzaldehydes (HODGSON and JENKINSON), 2272.

$C_7H_3O_6N_2Br$ Bromodinitrohydroxybenzaldehydes (HODGSON and JENKINSON), 2277.

$C_7H_3O_6N_2I$ Iododinitrohydroxybenzaldehydes (HODGSON and JENKINSON), 2279.

$C_7H_4O_2ClI$ 3-Chloro-5-iodobenzoic acid (MCALISTER and KENNER), 1915.

$C_7H_4O_2Cl_2S$ *o*-Sulphinobenzoic acid dichloride (PRICE and SMILES), 2861.

$C_7H_4O_2BrI$ 3-Bromo-5-iodobenzoic acid (MCALISTER and KENNER), 1915.
Bromoiodohydroxybenzaldehydes (HODGSON and JENKINSON), 2279.

$C_7H_4O_4NCl$ Chloronitrohydroxybenzaldehydes (HODGSON and JENKINSON), 2273.
5-Chloro-3-nitrosalicylaldehyde (LOVETT and ROBERTS), 1978.

$C_7H_4O_4NBr$ Bromonitrohydroxybenzaldehydes (HODGSON and JENKINSON), 2277.

$C_7H_4O_4NI$ *5-Iodo-3-nitrobenzoic acid* (MCALISTER and KENNER), 1914.
Iodonitrohydroxybenzaldehydes (HODGSON and JENKINSON), 2279.

$C_7H_4O_8N_5Br$ 4-Bromo-2:3:6-trinitrophenylmethylnitroamine (CLEMO and SMITH), 2422.

$C_7H_5O_2N_3S$ 2-Nitro-4-thiocyanoaniline (CHALLENGER and PETERS), 1372.

$C_7H_5O_2N_3Se$ 2-Nitro-4-selenocyanoaniline (CHALLENGER and PETERS), 1375.

$C_7H_5O_5N_4Br$ 4-Bromo-2:6-dinitrophenylmethylnitrosoamine (CLEMO and SMITH), 2421.

$C_7H_5O_7N_2As$ Nitrobenzoxazolone-5-arsinic acids (BALABAN), 3071.

$C_7H_6ON_2S$ 5-Methoxybenzene 2:1-diazosulphide (HODGSON and HANDLEY), 626.

$C_7H_6ON_3Cl$ 3-Chloroanisole-2-diazoimide (HODGSON and KERSHAW), 193.

$C_7H_6O_2NCl$ Nitrobenzyl chlorides, velocity of reaction of trimethylamine with (NORRISH and SMITH), 130.

$C_7H_6O_2NBr$ 5-Bromo-3-aminobenzoic acid (MCALISTER and KENNER), 1915.

$C_7H_6O_2NF$ *p*-Nitrobenzyl fluoride (C. K. and E. H. INGOLD), 2260.

$C_7H_6O_3NCl$ 5-Chloro-4-nitroso-3-hydroxyanisole (HODGSON and WIGNALL), 330.

$C_7H_6O_3NBr$ 2-Bromo-4-nitroanisole (BURNS, MCCOMBIE, and SCARBOROUGH), 2934.

$C_7H_6O_3NF$ Fluoronitrophenyl methyl ethers (HODGSON and NIXON), 1880.

$C_7H_6O_4NCl$ 5-Chloro-4-nitro-3-hydroxyanisole (HODGSON and WIGNALL), 330.

$C_7H_6O_4N_3Br$ *4-Bromo-2:6-dinitromethylaniline* (CLEMO and SMITH), 2421.

$C_7H_6O_5NAs$ Benzoxazolone-5-arsinic acid (BALABAN), 3071.

$C_7H_6O_8NAs$ 3-Nitro-4-hydroxy-5-carboxyphenylarsinic acid (NEWBERY, PHILLI and STICKINGS), 3062.

$C_7H_7O_2NCl_2$ 3-Chloro-5-aminobenzoic acid hydrochloride (MCALISTER and KI NER), 1915.

$C_7H_7O_2ClS$ *p*-Toluenesulphonyl chloride, parachor for (FREIMAN and SUGDE 267.

$C_7H_7O_2IS$ 2-Iodophenylmethylsulphone (BARBER and SMILES), 1144.

$C_7H_7O_3IS$ Iodotoluenesulphonic acids, and its salts (BARBER and SMILES), 114

$C_7H_7O_5SLi$ Benzaldehyde lithium hydrogen sulphate (FRIEND and POUNDE 2248.

$C_7H_7O_4N_2As$ 1-Aminobenzoxazole-4-arsinic acid (STICKINGS), 3133.

$C_7H_7O_4NSe$ 2-Nitro-*p*-tolueneseleninic acid (CHALLENGER and PETERS), 1369.

$C_7H_7O_5N_2As$ 6-Aminobenzoxazolone-5-arsinic acid (BALABAN), 3072.

C_7H_8ONCl 3-Chloro-2-aminoanisole, and its salts (HODGSON and KERSHAW), 1

C_7H_8OClP Phenylmethylphosphinyl chloride (GIBSON and JOHNSON), 96.

$C_7H_8O_2N_2S$ *6-Nitro-3-thioanisidine* (HODGSON *and* HANDLEY), 164.

$C_7H_8O_3N_3As$ 2-Aminobenziminazole-5-arsinic acid (STICKINGS), 3133.

$C_7H_8O_6NAs$ 3-Amino-4-hydroxy-5-carboxyphenylarsinic acid (NEWBERY, PH LIPS, and STICKINGS), 3062.

C_7H_8BrISe Phenyl methyl selenide bromo-iodide (EDWARDS, GAYTHWAI KENYON, *and* PHILLIPS), 2300.

$C_7H_9ON_2Cl$ 3-Chloroanisyl-2-hydrazine, hydrochloride of (HODGSON and KI SHAW), 193.

$C_7H_9O_4N_2As$ *p*-Carbamidophenylarsinic acid (STICKINGS), 3133.

$C_7H_9O_5N_2As$ 5-Carbamido-2-hydroxyphenylarsinic acid (STICKINGS), 3133.

$C_7H_{15}NCl_3As$ β-Piperidinoethyldichloroarsine hydrochloride (GOUGH and KIN 2436.

$C_7H_{15}NI_3As$ β-Piperidinoethyldi-iodoarsine hydriodide (GOUGH and KING), 24

$C_7H_{16}O_3NAs$ β-Piperidinoethylarsinic acid, and its hydrochloride (GOUGH KING), 2436.

$C_7H_{17}O_3N_2As$ γ-Piperazinopropylarsinic acid, and its dihydrochloride (GOUGH KING), 2445.

$C_7H_{17}NClI$ Methyl-β-chloroethyldiethylammonium iodide (GOUGH and KIN 2437.

7 V

$C_7H_3O_2N_2ClSe$ 2-Nitro-*p*-chlorophenyl selenocyanate (CHALLENGER and PETER 1371.

$C_7H_3O_2N_2BrS$ 4-Bromo-3-nitrophenyl thiocyanate (CHALLENGER and PETER 1373.

$C_7H_5O_4NBrI$ Bromoiodonitrohydroxybenzaldehydes (HODGSON and JENKINSO 2279.

$C_7H_6O_2NClS$ *3-Chloro-4-nitrothioanisole* (HODGSON and HANDLEY), 166.

$C_7H_6O_2ClIS$ Iodotoluenesulphonyl chlorides (BARBER and SMILES), 1144.

C_8 Group.

$C_8H_8O_3$ Anisic acid, condensation of chloral with (CHATTAWAY and CALVE 2913.

$C_8H_8Cl_2$ Dichloro-*o*-xylenes (HINKEL, AYLING, and BEVAN), 1874.

$C_8H_9N_3$ Dimethyl-1:2:3-benztriazoles (BRADY and REYNOLDS), 202.

C_8H_9Cl ω-Chloroxylene, nitration of (INGOLD and ROTHSTEIN), 1278.

C_8H_9Br ω-Bromoxylene, nitration of (INGOLD and ROTHSTEIN), 1278.
$C_8H_{10}O_3$ 1-Carboxy*cyclo*pentane-1-acetic anhydride (VOGEL), 2022.
*cyclo*Pentane-1-acetic-1-carboxylic anhydride (BARDHAN), 2600.
$C_8H_{10}O_8$ Diacetyltartaric acid, rotation dispersion of, and its esters (AUSTIN), 1825.
$C_8H_{12}O_2$ γ-Hydroxy-ααβ-trimethyl-Δβ-pentenoic lactone (BARDHAN), 2616.
β-*cyclo*Pentane*spiro*butyrolactone, and its silver salt (SIRCAR), 902.
$C_8H_{12}O_4$ α′-Hydroxy-ααβ-trimethylglutarolactone (BARDHAN), 2620.
Methyl caronate (HARIHARAN, MENON, and SIMONSEN), 438.
*cyclo*Pentylmalonic acid (VOGEL), 2022.
α-*iso*Propylglutaconic acids, isomeric (HARIHARAN, MENON, and SIMONSEN), 431.
Acid, and its salts, from oxidation of α-phellandrene (HENRY and PAGET), 77.
$C_8H_{12}O_5$ α-*iso*Propylacetonedicarboxylic acid (HARIHARAN, MENON, and SIMONSEN), 436.
$C_8H_{14}O_2$ ββ-Diethylbutyrolactone, and its silver salt (SIRCAR), 901.
β-Methyl-β-ethylvalerolactone, and its silver salt (SIRCAR), 903.
ααβ-Trimethyl-Δβ-pentenoic acid, and its silver salt (BARDHAN), 2615.
$C_8H_{14}O_3$ αββ-Trimethyl-lævulic acid (BARDHAN), 2618.
$C_8H_{14}O_4$ Suberic acid, catalytic decomposition of (VOGEL), 2032.
$C_8H_{14}O_5$ ββ′-Diacetoxyethyl ether (MACLEOD), 3092.
Trimethyl-δ-lyxonolactone (HIRST and SMITH), 3152.
Trimethyl γ-xylonolactone (HAWORTH and PORTER), 617.
$C_8H_{16}O_3$ *n*-Hexyloxyacetic acid (RULE, HAY, and PAUL), 1356.
$C_8H_{16}O_5$ Trimethyl lyxose (HIRST and SMITH), 3151.
$C_8H_{17}N$ *2:2:6-Trimethylpiperidine, and its salts* (GOUGH and KING), 2444.
$C_8H_{18}O_5$ Trimethyl methyl-lyxoside (HIRST and SMITH), 3151.

8 III

$C_8H_2N_2Cl_6$ ααβ-Trichloro-β-2:4:6-trichlorobenzeneazoethylene (CHATTAWAY and DALDY), 2760.
$C_8H_3N_2Cl_5$ αα-Dichloro-β-2:4:6-trichlorobenzeneazoethylene (CHATTAWAY and DALDY), 2758.
$C_8H_3N_2Cl_7$ Chloral ω-chloro-2:4:6-trichlorophenylhydrazone (CHATTAWAY and DALDY), 2760.
$C_8H_4N_2S_2$ *p*-Dithiocyanobenzene, preparation and nitration of (CHALLENGER and PETERS), 1371.
$C_8H_5O_3N_3$ ω-Diazo-*p*-nitroacetophenone (BRADLEY and SCHWARZENBACH), 2907.
$C_8H_5O_4Br$ 4-Bromophthalic acid, preparation of (BAKER), 2829.
$C_8H_5O_9N_5$ Tetranitroacetanilide (FLÜRSCHEIM and HOLMES), 3046.
$C_8H_6ON_2$ Diazoacetophenone (BRADLEY and ROBINSON), 1316.
$C_8H_6OCl_2$ ω-Chloro-*m*-toluoyl chloride (TITLEY), 2582.
$C_8H_6OBr_2$ ω-Bromo-*p*-toluoyl bromide (TITLEY), 2581.
$C_8H_6O_2N_2$ *2:3-Dihydroxyquinoxaline*, and its sodium salt (PHILLIPS), 2397.
$C_8H_6O_3N_2$ 5-Nitroethenyl-*o*-aminophenol (NEWBERY and PHILLIPS), 121.
$C_8H_6O_4N_2$ Nitro-3-hydroxy-1:4-benz*iso*oxazines (NEWBERY and PHILLIPS), 3046.
$C_8H_6O_6N_2$ Methyl 2:3-dinitrobenzoate (BRADY, DAY, and ALLAM), 981.
$C_8H_7O_2N_3$ 1-Acetoxy-1:2:3-benztriazole (BRADY and REYNOLDS), 197.
$C_8H_7O_3I$ 2-Iodo-3-methoxybenzoic acid (KENNER and TURNER), 2341
C_8H_7NS 1-Methylbenzthiazole, salts of (CLARK), 2315.
C_8H_7NSe 1-Methylbenzselenazole, and its salts (CLARK), 2316.
$C_8H_8ON_2$ 5-Aminoethenyl-*o*-aminophenol (NEWBERY and PHILLIPS), 122.

$C_8H_8OCl_2$ Dichloro-o-4-xylenols (HINKEL, AYLING, and BEVAN), 2532.

$C_8H_8O_2N_2$ 3-Amino-3-hydroxy-1:4-benzisooxazine, and its hydrochloride (BALABAN), *3070.*

Amino-3-hydroxy-1:4-benzisooxazines, and their salts (NEWBERY and PHILLIPS), 3048.

$C_8H_8O_2Se$ p-Carboxyphenyl methyl selenide (GAYTHWAITE, KENYON, and PHILLIPS), 2286.

$C_8H_8O_3Se$ p-Carboxyphenyl methyl selenoxide (GAYTHWAITE, KENYON, and PHILLIPS), 2286.

$C_8H_8O_4N_2$ *Dinitroethylbenzenes (BRADY, DAY, and ALLAM), 980.*

6-Nitro-2-acetamidophenol (NEWBERY and PHILLIPS), 3050.

$C_8H_8O_4Ni$ Methyl hydroxynickelosalicylate (DOAK and PACKER), 2768.

$C_8H_8O_8N_4$ 2:4:6-Trinitro-5-aminoresorcinol dimethyl ether (FLÜRSCHEIM and HOLMES), 3044.

$C_8H_9ON_3$ *1:6-Dimethyl-1:2:3-bentriazole 1-oxide (BRADY and REYNOLDS), 201.*

1-Methoxy-6-methyl-1:2:3-benztriazole (BRADY and REYNOLDS), 201.

C_8H_9OCl 3-Chloro-o-4-xylenol (HINKEL, AYLING, and BEVAN), 2531.

C_8H_9OBr β-Hydroxy-β-phenylethyl bromide (READ and REID), 1488.

$C_8H_9O_3S$ α- and β-Phenylethanesulphonic acids, barium salts (ASHWORTH and BURCKHARDT), 1798.

$C_8H_9O_4N_3$ Dinitro-4-aminoethylbenzenes (BRADY, DAY, and ALLAM), 981.

$C_8H_9NCl_2$ Dichloro-o-xylidines (HINKEL, AYLING, and BEVAN), 1876.

$C_8H_{10}O_2N_2$ Ethyl urocanate, picrate of (HUBBALL and PYMAN), 26.

$C_8H_{10}O_2S$ Benzylmethylsulphone, parachor for (FREIMAN and SUGDEN), 267.

$C_8H_{10}O_2S_2$ *Dimethylthiolbenzene disulphoxides (BELL and BENNETT), 3191.*

$C_8H_{10}N_2Cl_2$ Dichlorodiamino-o-xylenes (HINKEL, AYLING, and BEVAN), 1877.

$C_8H_{10}Br_2Se$ Phenyl ethyl selenide dibromide (EDWARDS, GAYTHWAITE, KENYON, and PHILLIPS), 2302.

$C_8H_{11}ON$ 3-Amino-o-4-xylenol (HINKEL, AYLING, and BEVAN), 2531.

$C_8H_{11}O_2P$ *Methyl phenylmethylphosphinate (GIBSON and JOHNSON), 97.*

$C_8H_{11}N_2Cl$ Chloroaminodimethylanilines (CLEMO and SMITH), 2420.

$C_8H_{11}N_2Br$ 4-Bromo-2-aminodimethylaniline (CLEMO and SMITH), 2420.

$C_8H_{11}NS_2$ 2:4-Dimethylthiolaniline, and its hydrochloride (HODGSON and HANDLEY), 164.

$C_8H_{15}ON_3$ *Methylmesityl oxide semicarbazone (BARDHAN), 2614.*

$C_8H_{15}O_3Tl$ Ethyl thallium dimethyl acetoacetate (MENZIES, SIDGWICK, CUTCLIFFE, and FOX), 1290.

$C_8H_{18}O_2S$ n-Octanesulphinic acid, ferric salt (FENTON and INGOLD), 3130.

$C_8H_{16}O_2Pt$ Trimethylplatinum acetylacetone (MENZIES), 565.

$C_8H_{18}O_4S_2$ *Trional, parachor from (FREIMAN and SUGDEN), 269.*

8 IV

$C_8H_3N_2Cl_2Br_4$ αα-Dichloro-β-bromo-β-2:4:6-tribromobenzeneazoethylene (CHATTAWAY and DALDY), 2762.

$C_8H_3N_2Cl_3Br_3$ ααβ-Trichloro-β-2:4:6-tribromobenzeneazoethylene (CHATTAWAY and DALDY), 2762.

$C_8H_3N_2Cl_5Br$ αα-Dichloro-α-bromo-β-2:4:6-trichlorobenzeneazoethylene (CHATTAWAY and DALDY), 2760.

$C_8H_3N_2Cl_2Br_3$ αα-Dichloro-β-2:4:6-tribromobenzeneazoethylene (CHATTAWAY and DALDY), 2762.

$C_8H_4O_2N_2Cl_4$ Glyoxylic acid ω-chloro-2:4:6-trichlorophenylhydrazone (CHATTAWAY and DALDY), 2761.

$C_8H_4O_4N_3Br$ m-Nitrophenylbromocyanonitromethane (FLÜRSCHEIM and HOLMES), 476.

$C_8H_4N_2SSe$ *p*-Thiocyanoselenocyanobenzene, preparation and nitration of (CHALLENGER and PETERS), 1372.

$C_8H_5O_2N_2Cl_3$ Glyoxylic acid 2:4:6-trichlorophenylhydrazone (CHATTAWAY and DALDY), 2760.

$C_8H_5O_2N_2Br_3$ Glyoxylic acid 2:4:6-tribromophenylhydrazone (CHATTAWAY and DALDY), 2762.

C_8H_6ONCl 3-Chloro-2-cyanoanisole (HODGSON and KERSHAW), 192.

$C_8H_6O_2NCl$ ω-Chloronitrostyrenes, alkaline hydrolysis of (DANN, HOWARD, and DAVIES), 605.

$C_8H_6O_2NBr$ ω-Bromonitrostyrenes, alkaline hydrolysis of (DANN, HOWARD, and DAVIES), 605.

$C_8H_6O_2N_2S$ Nitro-*o*-tolyl thiocyanates (CHALLENGER and PETERS), 1368.

$C_8H_6O_2N_2Se$ Nitro-*p*-tolyl selenocyanates (CHALLENGER and PETERS), 1370.

$C_8H_6O_2ClI$ *Methyl 3-chloro-5-iodobenzoate* (*MCALISTER and KENNER*), *1915*.

$C_8H_6O_2BrI$ Methyl 3-bromo-5-iodobenzoate (MCALISTER and KENNER), 1915.

$C_8H_6O_3NAs$ 3-Hydroxy-1:4-benz*iso*oxazine 6-arsenoxide (NEWBERY, PHILLIPS, and STICKINGS), 3056.

$C_8H_6O_4N_2Cl_2$ Dichlorodinitro-*o*-xylenes (HINKEL, AYLING, and BEVAN), 1876.

$C_8H_6O_5N_3Cl$ 2:4-Dinitrophenylchloroacetamide (FAIRBOURNE and FAWSON), 1079.

$C_8H_6O_5N_3Br$ 2:4-Dinitrophenylbromoacetamide (FAIRBOURNE and FAWSON), 1079.

$C_8H_6O_6N_5Cl$ Chlorodinitrohydroxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 2274.

$C_8H_6O_6N_5Br$ Bromodinitrohydroxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 2277.

$C_8H_6O_6N_5I$ Iododinitrohydroxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 2279.

$C_8H_7O_2NCl_2$ *Dichloronitro-o-xylenes* (*HINKEL, AYLING, and BEVAN*), *1876*.

$C_8H_7O_3N_2As$ 8-Amino-3-hydroxy-1:4-benz*iso*oxazine 6-arsenoxide, hydrochloride of (NEWBERY, PHILLIPS, and STICKINGS), 3059.

$C_8H_7O_4N_2Cl$ 3-Nitro-2-chloroacetamidophenol (NEWBERY and PHILLIPS), 3048.

$C_8H_7O_4N_4Cl$ Chloronitrohydroxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 2273.

$C_8H_7O_4N_4Br$ Bromonitrohydroxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 2277.

$C_8H_7O_4N_4I$ Iodonitrohydroxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 2279.

$C_8H_7O_5N_2As$ 2:3-Dihydroxyquinoxalinearsinic acids (PHILLIPS), 3139.
2:4-Diketo-1:2:3:4-tetrahydro-1:3-quinazoline-7-arsinic acid (STICKINGS), 3134.
3-Nitro-4-hydroxy-5-acetamidophenylarsenoxide (NEWBERY and PHILLIPS), 2380.

$C_8H_7O_7N_2As$ Nitrohydroxy-1:4-benz*iso*oxazinearsinic acids (NEWBERY, PHILLIPS, and STICKINGS), 3057; (BALABAN), 3068.

C_8H_8ONCl *N*-Chloroacetanilide, decomposition of, by heat (BRADFIELD), 351.

C_8H_8ONBr *o*-Bromoacetanilide, *nitration of* (GIBSON and JOHNSON), 3092.

$C_8H_8ON_3Br$ *p*-Bromobenzaldehyde semicarbazone (INGOLD and SHOPPEE), 407.

$C_8H_8O_2NBr$ ω(1)-Bromo-3-nitro-*p*-xylene (INGOLD and ROTHSTEIN), 1220.

$C_8H_8O_2NAs$ 2:3-Dihydro-1:4-benz*iso*oxazine-6-arsenoxide (NEWBERY, PHILLIPS, and STICKINGS), 3064.

$C_8H_8O_2N_2S$ Benziminazole-2-thioglycollic acid (STEPHEN and WILSON), 1420.

$C_8H_8O_2Br_2Se$ *p*-Carboxyphenyl methyl selenide (GAYTHWAITE, KENYON, and PHILLIPS), 2286.
Phenylselenoglycollic acid dibromide (EDWARDS, GAYTHWAITE, KENYON, and

$C_8H_8O_3NCl$ 5-Chloro-3-nitro-*o*-4-xylenol (HINKEL, AYLING, and BEVAN), 2531.

$C_8H_8O_3NAs$ 5-Acetamido-2-hydroxyphenylarsenoxide (NEWBERY and PHILLIPS), 2380.

$C_8H_8O_4NCl$ 5-Chloro-2- and -4-nitroresorcinols (HODGSON and WIGNALL), 331.

$C_8H_8O_4N_3Br$ Bromodinitrodimethylanilines (CLEMO and SMITH), 2421.

$C_8H_8O_5NAs$ 3-Hydroxy-1:4-benz*iso*oxazinearsinic acids (NEWBERY, PHILLIPS, and STICKINGS), 3054.

$C_8H_8O_6NAs$ 3:7-Dihydroxy-1:4-benz*iso*oxazine-6-arsinic acid (NEWBERY, PHILLIPS, and STICKINGS), 3058.

$C_8H_8N_2Br_2S$ 5-Bromo-1-amino-3-methylbenzthiazole hydrobromide (HUNTER and STYLES), 3023.

$C_8H_8N_2Br_4S$ 1-Amino-3-methylbenzthiazole tetrabromide (HUNTER and STYLES), 3028.

5-Bromo-1-amino-3-methylbenzthiazole dibromide hydrobromide (HUNTER and STYLES), 3025.

C_8H_9OClS Chloro-5-methoxythioanisoles (HODGSON and HANDLEY), 627.

$C_8H_9O_2N_2Br$ Bromonitrodimethylanilines (CLEMO and SMITH), 2420.

$C_8H_9O_3N_2As$ 3-Amino-5-acetamido-4-hydroxyphenylarsenoxide, salts of (NEWBERY and PHILLIPS), 2377.

Methylbenziminazolearsinic acids (PHILLIPS), 3136.

$C_8H_9O_5NS$ Ethyl *p*-nitrobenzenesulphonate (BELL), 2776.

Nitro-5-methoxyphenylmethylsulphones (HODGSON and HANDLEY), 627.

$C_8H_9O_5N_2As$ Aminohydroxy-1:4-benz*iso*oxazinearsinic acids (NEWBERY, PHILLIPS, and STICKINGS), 3057; (BALABAN), 3069.

$C_8H_9O_7N_2As$ 3-Nitro-5-acetamido-2-hydroxyphenylarsinic acid (NEWBERY and PHILLIPS), 2376.

$C_8H_9O_8N_2As$ 2-Nitro-4-ω-hydroxyacetamido-3-hydroxyphenylarsinic acid (BALABAN), 3069.

$C_8H_9N_2BrS$ 1-Amino-3-methylbenzthiazole hydrobromide (HUNTER and STYLES), 3028.

$C_8H_9N_2Br_3S$ 1-Amino-3-methylbenzthiazole dibromide hydrobromide (HUNTER and STYLES), 3022.

$C_8H_{10}ONCl$ Chloroamino-*o*-4-xylenols (HINKEL, AYLING, and BEVAN), 2531.

$C_8H_{10}O_2NAs$ Acetamidohydroxyphenylarsines (NEWBERY and PHILLIPS), 2381.

$C_8H_{10}O_4NAs$ 2:3-Dihydro-1:4-benz*iso*oxazine-6-arsinic acid (NEWBERY, PHILLIPS, and STICKINGS), 3063.

$C_8H_{10}O_5NAs$ 3-Hydroxy-1:4-benz*iso*oxazine-7-arsinic acid (BALABAN), 3068.

$C_8H_{10}O_6NAs$ 5-Acetamido-2:4-dihydroxyphenylarsinic acid (NEWBERY, PHILLIPS, and STICKINGS), 3058.

$C_8H_{11}O_5N_2As$ 2-Amino-4-acetamido-3-hydroxyphenylarsinic acid, and its salts (BALABAN), 812.

3-Amino-5-acetamidohydroxyphenylarsinic acids (NEWBERY and PHILLIPS), 2376.

$C_8H_{11}O_6N_2As$ 2-Amino-4-ω-hydroxyacetamido-3-hydroxyphenylarsinic acid (BALABAN), 3069.

$C_8H_{14}O_2N_2S$ Ethyl 1:4:5:6-tetrahydropyrimidine-2-thioglycollate (STEPHEN and WILSON), 1420.

$C_8H_{18}O_3NAs$ γ-Piperidinopropylarsinic acid, and its hydrochloride (GOUGH and KING), 2443.

$C_8H_{20}OI_2Te_2$ Diethyltelluronium α-oxyiodide (GILBERT and LOWRY), 3183.

$C_8H_{20}O_6N_2As_2$ *NN'*-Piperazine-di-ββ'-ethylarsinic acid and its dihydrochloride (GOUGH and KING), 2436.

8 V

$C_8H_3O_2N_3SSe$ 2-Nitro-4-thiocyanophenyl selenocyanate (CHALLENGER and PETERS), 1373.

$C_8H_4O_3N_8S_8Mo$ Tetrahydrogen dimolybdenum trioxyoctathiocyanate, salts of (JAMES and WARDLAW), 2733.

C_8H_6ONClS 3-Chloro-2-thiocyanoanisole (HODGSON and KERSHAW), 192.

$C_8H_6ONCl_2I$ 2:4-Dichloro-6-iodoacetanilide (BRADFIELD, ORTON, and ROBERTS), 783.

$C_8H_6ONCl_2F$ 3-Fluoro-4:6-dichloroacetanilide (INGOLD and VASS), 422.

$C_8H_6O_3N_2ClI$ Chloroiodo-6-nitroacetanilides (BRADFIELD, ORTON, and ROBERTS), 784.

$C_8H_6O_3N_2BrI$ Bromoiodo-6-nitroacetanilides (BRADFIELD, ORTON, and ROBERTS), 784.

$C_8H_6O_5NCl_2As$ 2-*Nitrophenoxyacetic* acid 4-*dichloroarsine* (NEWBERY, PHILLIPS, and STICKINGS), 3056.

C_8H_7ONBrI 2-Bromo-4-iodoacetanilide (BRADFIELD, ORTON, and ROBERTS), 783.

C_8H_7ONClF 3-Fluoro-6-chloroacetanilide (INGOLD and VASS), 422.

$C_8H_7O_5NClAs$ 8-Chloro-3-hydroxy-1:4-benzoxazine-6-arsinic acid (NEWBERY, *PHILLIPS, and STICKINGS*), *3060*.

$C_8H_8O_2NCl_2As$ Acetamidohydroxyphenyldichloroarsines (NEWBERY and PHILLIPS), 2380.

$C_8H_8O_3N_2ClAs$ 8-Amino-3-hydroxy-1:4-benz*iso*oxazine-6-hydroxychloroarsine, hydrochloride of (NEWBERY, PHILLIPS, and STICKINGS), 3059.

$C_8H_8O_7N_2ClAs$ 3-Nitro-5-chloroacetamido-4-hydroxyphenylarsinic acid (NEWBERY, PHILLIPS, and STICKINGS), 3059.

$C_8H_9O_2N_2Cl_2As$ *3-Amino-5-acetamido-4-hydroxyphenyldichloroarsine*, hydrochloride of (NEWBERY and PHILLIPS), 2377.

$C_8H_9O_2N_2I_2As$ 3-Amino-5-acetamido-4-hydroxyphenyldi-iodoarsine, hydriodide of (NEWBERY and PHILLIPS), 2377.

$C_8H_9O_4NClAs$ 3-Chloro-6-acetamidophenylarsinic acid, and its magnesium salt (BALABAN), 812.

$C_8H_{10}O_4N_2ClAs$ 6-Glycineamide-3-chlorophenylarsinic acid, and its salts (BALABAN), 813.

$C_8H_{24}ON_2Cl_5Mo$ Bisdiethylammonium molybdenyl pentachloride (JAMES and WARDLAW), 2737.

Ditetramethylammonium molybdenyl pentachloride (JAMES and WARDLAW), 2737.

8 VI

$C_8H_6ONClBrI$ Chlorobromoiodoacetanilides (BRADFIELD, ORTON, and ROBERTS), 783.

C_9 Group.

$C_9H_6O_2$ *Phenylpropiolic acid, addition of bromine and chlorine to* (HANSON and JAMES), 2979.

$C_9H_8O_2$ Cinnamic acid, addition of mixtures of bromine and chlorine to (HANSON and JAMES), 1955.

$C_9H_8O_4$ Homophthalic acid, action of phosphorus pentachloride on (DAVIES and POOLE), *1816 ; copper salt (POOLE), 1379.*

4-Methoxy*iso*phthalaldehydic acid (CHATTAWAY and CALVET), 2916.

Phthalic acid, separation of homophthalic acid from (POOLE), 1378.

$C_9H_8O_5$ 4-Methoxy*iso*phthalic acid (CHATTAWAY and CALVET), 2916.

$C_9H_{10}O_2$ *5-cyclo*Pentane*spirocyclo*penten-3-ol-1:4-dione (GOSS), 1808.

$C_9H_{10}O_5$ Methyl hydrogen 5-methyl*dicyclo*penten-3-oldicarboxylate (GOSS and INGOLD), 1278.

$C_9H_{12}O_3$ *cyclo*Pentylideneacetoacetic acid (JUPP, KON, and LOCKTON), 1642.

$C_9H_{14}O$ α-Methyl-$Δ^1$-*cyclo*pentenylacetone (BARDHAN), 2604.

α-Methyl*cyclo*pentylideneacetone (BARDHAN), *2603.*

Phorone, ring-chain tautomerism in derivatives of (SUGDEN), 410.

$C_9H_{14}O_2$ *cyclo*Hexane*spiro*butyrolactone, and its silver salt (SIRCAR), *57*, *902*.
*β-cyclo*Hexylacrylic acid, and its salts (SIRCAR), 55.
*β-cyclo*Pentane*spiro*valerolactone, and its silver salt (SIRCAR), 903.
$C_9H_{14}O_3$ 1-Acetyl*cyclo*pentane-1-acetic acid (BARDHAN), 2601.
$C_9H_{14}O_4$ Methyl *cyclo*pentane-1-acetic-1-carboxylate (BARDHAN), 2600.
$C_9H_{14}O_6$ αα-Dihydroxy*cyclo*pentane-1:1-diacetic acid (GOSH), 1310.
$C_9H_{14}N_2$ αγ-Diamino-β-phenylpropane, and its salts (JACKSON and KENNEI 1658.
$C_9H_{16}O_2$ Allyl hexoate (DEULOFEU), 528.
ββ-Diethylvalerolactone, and its silver salt (*SIRCAR*), 903.
Hydroxy-2:2:3:3-tetramethyl*cyclo*pentanone (SHOPPEE), 1666.
$C_9H_{18}O_3$ *n*-Heptyloxyacetic acid (RULE, HAY, and PAUL), 1356.

9 III

$C_9H_4O_2Cl_4$ 3:3:4:4-Tetrachloro-3:4-dihydro*iso*coumarin (DAVIES and POOLI 1620.
$C_9H_5O_2Cl$ 3-Chloro*iso*coumarin (DAVIES and POOLE), 1618.
$C_9H_5N_2Br_3$ 2-ω-Tribromomethylquinoxaline (BENNETT and WILLIS), 1974.
$C_9H_6O_2Cl_4$ ααββ-Tetrachloro-β-phenylpropionic acid (HANSON and JAMES 2985.
$C_9H_7O_2N$ Methyl *o*-cyanobenzoate, action of magnesium phenyl bromide on (BOY and LADHAMS), 2089.
$C_9H_7O_3N$ *Methylphthaloximes* (*BRADY, BAKER, GOLDSTEIN*, and *HARRIS* 539.
$C_9H_8O_2N_2$ *o*-Phenylenemalonamide, *sodium salt* (*PHILLIPS*), 2398.
C_9H_8ClBr *p*-Chlorocinnamyl bromide (BURTON), 1656.
C_9H_9OCl *p*-Chlorocinnamyl alcohol (BURTON), 1655.
α-*p*-Chlorophenylallyl alcohol (BURTON), 1655.
$C_9H_9O_2N_3$ 1-Acetoxy-6-methyl-1:2:3-benztriazole (BRADY and REYNOLDS), 200.
$C_9H_9O_6N_3$ *O*-Methyl-3:5-dinitro-4-methoxybenzaldoxime (BRADY and MILLER 341.
C_9H_9NS 1-Ethylbenzthiazole, and its picrate (CLARK), 2319.
C_6H_9NSe 2-Methyl-1-methylenebenzselenazoline (CLARK), 2317.
$C_9H_{10}O_2S$ *m*-Ethylthiolbenzoic acid (HOLLOWAY, KENYON, and *PHILLIPS* 3003.
$C_9H_{10}O_3N_2$ 2-Aminomalonanilic acid (*PHILLIPS*), 2398.
$C_9H_{10}O_2N_4$ 3:3′-Dimethyl-5:5′-dipyrazolonyl 1:1′-ketone (MUNRO and WILSON 1260.
$C_9H_{10}O_3S$ Carboxyphenyl ethyl sulphoxide, and its resolution (HOLLOWAY KENYON, and PHILLIPS), 3003.
$C_9H_{10}O_4S$ *m*-Carboxyphenylethylsulphone (HOLLOWAY, KENYON, and PHILLIPS 3004.
$C_9H_{10}O_4Cu$ Methyl methoxycuprisalicylate (DOAK and PACKER), 2767.
$C_9H_{10}O_4Ni$ Methyl methoxynickelosalicylate (DOAK and PACKER), 2768.
$C_9H_{10}N_2S$ 1-Methylamino-3-*methylbenzthiazole* (*HUNTER and STYLES*), 3025.
$C_9H_{11}O_2N_3$ Aldehydomethylphenol semicarbazones (BELL and HENRY), 2222.
$C_9H_{11}O_2Tl$ *Thallium dimethyl salicylaldehyde* (*MENZIES, SIDGWICK, CUTCLIFFE*, and FOX), 1291.
$C_9H_{12}O_2Cl_2$ 1:1-*Dichloro*-2:2:3:3-tetramethyl*cyclo*pentanedione (INGOLD and SHOPPEE), 408.
$C_9H_{12}O_3S$ Ethyl *p*-toluenesulphonate, parachor for (FREIMAN and SUGDEN), 267.
$C_9H_{12}N_2S$ *o*-Tolylmethylthiocarbamides (HUNTER and STYLES), 3024.
$C_9H_{13}ON$ *p*-Dimethylaminobenzyl alcohol (CLEMO and S———
[illegible].

$C_9H_{13}ON$ Nor-*d*-ψ-ephedrine, and its salts (SMITH), 51.

$C_9H_{13}O_2Cl$ 1-Chloro-2:2:3:3-tetramethyl-[0,1,2]-*dicyclo*pentan-4-ol-5-one (INGOLD and SHOPPEE), 408.

$C_9H_{13}O_2P$ Ethyl phenylmethylphosphinate (GIBSON and JOHNSON), 96.

$C_9H_{14}ON_2$ αγ-Diamino-β-*p*-hydroxyphenylpropane, and its dihydrobromide (JACKSON and KENNER), 1661.

3:3:4:4-Tetramethyl*cyclo*pentane-1:2-dione *furazan* (INGOLD and SHOPPEE), 396.

$C_9H_{14}OBr_2$ Dibromotetramethyl*cyclo*pentanone (SHOPPEE), 2363.

$C_9H_{14}O_2N_2$ αγ-Diamino-β-3:4-dihydroxyphenylpropane, and its dihydrobromide (JACKSON and KENNER), 1661.

$C_9H_{14}O_3N_2$ 4:4:5:5-Tetramethyl*cyclo*pentanetrione 1:3-dioxime (INGOLD and SHOPPEE), 391.

$C_9H_{15}ON$ β-*cyclo*Hexylacrylamide (SIRCAR), 55.

$C_9H_{15}OP$ Phenyltrimethylphosphonium hydroxide, picrate of (INGOLD, SHAW, and WILSON), 1283.

$C_9H_{15}OSb$ Phenytrimethylstibonium hydroxide, picrate of (INGOLD, SHAW, and WILSON), 1283.

$C_9H_{15}O_2N$ 2:2:3:3-Tetramethyl-[0, 1, 2]-*dicyclo*pentan-4-ol-5-*one oximes* (INGOLD and SHOPPEE), 394.

ααββ-Tetramethylglutarimide (INGOLD and SHOPPEE), 396.

Lactam of δ-amino-α-keto-γγ-dimethyl*iso*heptoic acid (INGOLD and SHOPPEE), 400.

Lactam of δ-amino-α-keto-ββγγ-tetramethylvaleric acid (INGOLD and SHOPPEE), 395.

$C_9H_{15}O_3N$ 1-Acetyl*cyclo*pentane-1-acetic acid oxime (BARDHAN), 2601.

Substance, from potassium cyanide and methylmesityl oxide (BARDHAN), 2614.

$C_9H_{15}O_3N_3$ 4:4:5:5-Tetramethyl*cyclo*pentanetrione 1:2:3-trioxime (INGOLD and SHOPPEE), 392.

$C_9H_{16}O_2N_2$ *3:3:4:4-Tetramethylcyclopentane-1:2-dione* dioxime (INGOLD and SHOPPEE), 396.

$C_9H_{16}O_4S_2$ Pentane-αε-dithiolacetic acid (CHIVERS and SMILES), 701.

$C_9H_{17}ON$ 4:4:5:5-Tetramethyl*cyclo*pentanetrione *oxime* (INGOLD and SHOPPEE), 392.

Tetramethyl*cyclo*pentanone oxime (INGOLD and SHOPPEE), 398.

$C_9H_{17}ON_3$ γδ-Dimethylhexen-β-one semicarbazones (ABBOTT, KON, and SATCHELL), 2517.

ε-Methylhepten-γ-one semicarbazones (ABBOTT, KON, and SATCHELL), 2523.

$C_9H_{17}O_2Tl$ Thallium diethyl acetylacetone (MENZIES, SIDGWICK, CUTCLIFFE, and FOX), 1289.

$C_9H_{17}O_3N_3$ *αββ-Trimethyl-lævulic acid semicarbazone* (BARDHAN), 2613.

$C_9H_{17}O_{12}N_3$ Triaminopropane trihydrogen trioxalate (MANN), 898.

$C_9H_{19}O_2N$ Hydroxy-*2:2:3:3-tetramethylcyclo*pentylamines, picrates of (INGOLD and SHOPPEE), 400, 404.

Tetramethyl*cyclo*pentylamines, and their salts (INGOLD and SHOPPEE), 392, 398.

9 IV

C_9H_4OClBr 3-Chloro-2-bromo-1-ketoindene (HANSON and JAMES), 2983.

$C_9H_6O_2ClBr$ Chlorobromocinnamic acid (HANSON and JAMES), 2983.

$C_9H_6O_2Cl_3Br$ *αββ-Trichloro-α-bromo-β-phenylpropionic* acid (HANSON and JAMES), 2985.

$C_9H_6O_3NCl_3$ αββ-Trichloro-5-nitro-2-methoxystyrene (CHATTAWAY and CALVET), 2917.

$C_9H_7O_3NCl_4$ 5-Nitro-2-methoxy-1-αβββ-tetrachloroethylbenzene (CHATTAWAY and

$C_9H_7O_3N_3S$ 2-Nitro-4-thiocyanoacetanilide (CHALLENGER and PETERS), 1372.

$C_9H_7O_3N_3Se$ 2-Nitro-4-selenocyanoacetanilide (CHALLENGER and PETERS), 1373.

$C_9H_8O_2ClBr$ β-Chloro-α-bromo-β-phenylpropionic acid (HANSON and JAMES), 1958

$C_9H_8O_3NCl$ 3-Chloro-5-acetamidobenzoic acid (McALISTER and KENNER), 1915.

$C_9H_8O_3NBr$ 3-Bromo-5-acetamidobenzoic acid (McALISTER and KENNER), 1915.

$C_9H_8O_4NI$ Ethyl 5-iodo-3-nitrobenzoate (McALISTER and KENNER), 1914.

$C_9H_8O_7NAs$ 3-Hydroxy-8-carboxy-1:4-benz*iso*oxazine-6-arsinic acid (NEWBERY PHILLIPS, and STICKINGS), 3062.

$C_9H_9O_5N_2As$ 6-Acetamidobenzoxazolonearsinic acids (BALABAN), 3072.

$C_9H_{10}O_2NCl$ Acetyl derivative of 3-chloro-2-aminoanisole (HODGSON and KERSHAW), 192.

$C_9H_{10}O_2SBr_2$ *m*-Carboxyphenyl ethyl sulphide and dibromide (HOLLOWAY KENYON, and PHILLIPS), 3004.

$C_9H_{10}O_5NAs$ Hydroxymethyl-1:4-benz*iso*oxazinearsinic acids (NEWBERY, PHILLIPS, and STICKINGS), 3061.

$C_9H_{10}O_5N_2As$ 1-Amino-6-acetamidobenzoxazole-4-arsinic acid (STICKINGS), 3134.

$C_9H_{10}O_7NAs$ 3-Acetamido-4-hydroxy-5-carboxyphenylarsinic acid (NEWBERY PHILLIPS, and STICKINGS), 3062.

$C_9H_{10}N_2Br_4S$ *s*-*o*-Tolylmethylthiocarbamide tetrabromide (HUNTER and STYLES 3024.

$C_9H_{11}O_2N_2Cl$ 5-Chloro-4-nitroso-3-methoxydimethylaniline (HODGSON and WIGNALL), 332.

$C_9H_{11}O_3N_2As$ 2-Ethylbenziminazolearsinic acid (PHILLIPS), 3137.

$C_9H_{11}O_4N_2As$ 2-α-Hydroxyethylbenziminazolearsinic acids (PHILLIPS), 3137.

$C_9H_{11}N_2Br_3S$ *s*-*o*-Tolylmethylthiocarbamide tribromide (HUNTER and STYLES 3024

$C_9H_{12}ONCl$ 5-Chloro-3-methoxydimethylaniline (HODGSON and WIGNALL), 331.

$C_9H_{12}O_2ClBr$ 1-Chloro-1-bromo-2:2:3:3-tetramethyl*cyclo*pentanedione (INGOLD and SHOPPEE), 409.

$C_9H_{14}O_2NAs$ *m*-Nitrophenyltrimethylarsonium hydroxide, picrate of (INGOLD SHAW, and WILSON), 1285.

$C_9H_{14}O_2NP$ *m*-Nitrophenyltrimethylphosphonium hydroxide, picrate of (INGOLD SHAW, and WILSON), 1283.

$C_9H_{14}O_2NSb$ *m*-Nitrophenyltrimethylstibonium hydroxide, picrate of (INGOLD SHAW, and WILSON), 1285.

$C_9H_{21}NCl_2As$ γ-*n*-Hexylaminopropyldichloroarsine hydrochloride (GOUGH and KING), 2443.

9 V

$C_9H_6OClBrN$ 3-Chloro-2-bromo-1-ketoindene oxime (HANSON and JAMES), 2984.

$C_9H_{10}ONClS$ Chlorothioacetanisidines (HODGSON and HANDLEY), 163, 166.

$C_9H_{11}O_3NClAs$ Acetamidohydroxyphenylmethoxychloroarsines (NEWBERY and PHILLIPS), 2380.

$C_9H_{11}O_4NClAs$ 3-ω-Chlorocarbethoxyamino-4-hydroxyphenylarsinic acid (NEWBERY, PHILLIPS, and STICKINGS), 3063.

C_{10} Group.

$C_{10}H_{16}$ Limonene, oxidation of (HENRY and PAGET), 75.
α-Phellandrene, oxidation of (HENRY and PAGET), 72.

10 II

$C_{10}H_8O_5$ 4:5-Methylenedioxyhomophthalic anhydride (STEVENS and WILSON

$C_{10}H_{8}O_{4}$ β-o-Carboxyphenylpropionic acid (TITLEY), 2575.

$C_{10}H_{8}O_{6}$ 5-Carboxy-2-methoxyphenylglyoxylic acid (CHATTAWAY and CALVET), 2917.

$C_{10}H_{9}N_{3}$ Glyoxaline-4(5)-methylideneaniline (HUBBALL and PYMAN), 25.

$C_{10}H_{10}O_{2}$ Benzylmethylglyoxal, absorption spectra of (LOWRY, MOUREU, and MACCONKEY), 3167.

Hydroxystyryl methyl ketones (McGOOKIN and SINCLAIR), 1174.

$C_{10}H_{10}O_{4}$ Carboxyphenylpropionic acids (TITLEY), 2581.

ω-Hydroxy-4-acetoxyacetophenone (ROBERTSON and ROBINSON), 1465.

$C_{10}H_{10}O_{5}$ ω-Hydroxy-4-methylcarbonatoacetophenone (ROBERTSON and ROBINSON), 1465.

$C_{10}H_{11}Br$ 4-Methylcinnamyl bromide (BURTON and INGOLD), 915.

$C_{10}H_{12}O$ 4-Methylcinnamyl alcohol (BURTON and INGOLD), 915.

$C_{10}H_{12}O_{3}$ 3-Methoxy-5-*cyclo*pentane*spirocyclo*penten-1:4-dione (GOSS), 1308.

$C_{10}H_{12}O_{4}$ 4-Hydroxy-3:5-dimethoxyacetophenone (BRADLEY and ROBINSON), 1564.

5-*cyclo*Pentane*spirodicyclo*pentan-4-ol-3-one-1-carboxylic acid (GOSS), 1309.

$C_{10}H_{13}Br$ o-Bromo-*tert.*-butylbenzene (SHOESMITH and MACKIE), 2339.

$C_{10}H_{13}I$ Iodo-*tert.*-butylbenzenes (SHOESMITH and MACKIE), 2338.

$C_{10}H_{14}O_{3}$ Camphoric anhydride, action of substituted aromatic amines on (SINGH, AHUJA, and LAL), 2410.

Δ^{1}-*cyclo*Hexenylacetoacetic acid (JUPP, KON, and LOCKTON), 1640.

α-Methyl*cyclo*pentane-1:1-diacetic anhydride (BARDHAN), 2597.

$C_{10}H_{14}O_{4}$ α-Hydroxy-α-methyl*cyclo*pentane-1:1-diacetolactone, and its salts (BARDHAN), 2598.

$C_{10}H_{16}O$ *l*-Carene oxide (PILLAY and SIMONSEN), 363.

$C_{10}H_{16}O_{2}$ β-*cyclo*Hexane*spiro*valerolactone, and its silver salt (SIRCAR), 903.

Methyl β-*cyclo*hexylacrylate (SIRCAR), 55.

Methyl derivative of 2:2:3:3-tetramethyl-[0, 1, 2] *dicyclo*pentan-4-ol-5-one (INGOLD and SHOPPEE), 389.

$C_{10}H_{16}O_{3}$ Methyl 1-acetyl*cyclo*pentane-1-acetate (BARDHAN), 2601.

Substance, from oxidation of α-phellandrene (HENRY and PAGET), 77.

$C_{10}H_{16}O_{4}$ *cyclo*Heptylmalonic acid (VOGEL), 2025.

α-Methyl*cyclo*pentane-1:1-diacetic acid, and its silver salt (BARDHAN), 2597.

$C_{10}H_{16}O_{5}$ Methyl hydrogen γγ-dihydroxy-ααββ-tetramethylglutarate lactone (INGOLD and SHOPPEE), 406.

$C_{10}H_{18}O_{2}$ *d*-Carene-β-glycol (PILLAY and SIMONSEN), 362.

Methoxy-2:2:3:3-tetramethyl*cyclo*pentanone (INGOLD and SHOPPEE), 402; (SHOPPEE), 1670.

$C_{10}H_{18}O_{3}$ Ethyl αββ-trimethyl-lævulate (BARDHAN), 2613.

$C_{10}H_{20}O_{3}$ Ethyl β-hydroxy-ααβ-trimethyl-n-valerate (BARDHAN), 2615.

n-Octyloxyacetic acid (RULE, HAY, and PAUL), 1357.

10 III

$C_{10}H_{2}O_{3}Cl_{6}$ 5:7-Dichloro-6-hydroxy-2:4-bisdichloromethylene-1:3-benzdioxin (CHATTAWAY and CALVET), 2918.

$C_{10}H_{4}O_{3}Cl_{8}$ 5:7-Dichloro-6-hydroxy-2:4-bistrichloromethyl-1:3-benzdioxin (CHATTAWAY and CALVET), 2918.

$C_{10}H_{6}N_{2}Br_{4}$ 2:3-Di(ω-dibromomethyl)quinoxaline (BENNETT and WILLIS), 1974.

$C_{10}H_{6}S_{2}Ni$ Nickel 1:8-dithiolnaphthalene (PRICE and SMILES), 2374.

$C_{10}H_{7}OBr$ 3-Bromo-β-naphthol (CLEMO and SPENCE), 2819.

C[illegible]H[illegible]O[illegible]Cl[illegible] 5-Carboxy-2-methoxy-1-αβββ-tetrachloroethylbenzene (CHATTAWAY

$C_{10}H_8O_3Br_2$ Dibromo-3-methoxycinnamic acid (H. and W. DAVIES), 604.

$C_{10}H_8O_5S_2$ 1-Sulphinonaphthalene-8-sulphonic acid, and its sodium salt (PRICE and SMILES), 2373.

$C_{10}H_8NCl$ 2-Chloro-6-methylquinoline (HAMER), 210.

$C_{10}H_9OCl$ *3-Chlorostyryl methyl ketone* (HEILBRON and HILL), 2868*a*.

$C_{10}H_9O_2N_3$ 3:4-Diformamidobenzyl cyanide (PHILLIPS), 2396.

$C_{10}H_9O_3N$ Indoxylacetic acid (JACKSON and KENNER), 580.

$C_{10}H_9O_3Br$ 6-Bromo-3-methoxycinnamic acid (H. and W. DAVIES), 603.

$C_{10}H_9O_4Cl_3$ 5-Carboxy-2-methoxy-1-βββ-trichloro-α-hydroxyethylbenzene (CHATTAWAY and CALVET), 2915

$C_{10}H_9O_5N$ *p*-Nitro-ω-acetoxyacetophenone (BRADLEY and SCHWARZENBACH), 2907.

$C_{10}H_9NI_2$ *2-Iodoquinoline methiodide* (HAMER), 209.

$C_{10}H_{10}O_2Br_2$ Ethyl ωω-dibromo-*p*-toluate (TITLEY), 2581.
Safrole *di*bromide (READ and REID), 1490.

$C_{10}H_{10}O_3N_2$ 8-Acetylamino-3-hydroxy-1:4-benz*iso*oxazine (BALABAN), 3070.
Acetylamino-3-hydroxy-1:4-benz*iso*oxazines (NEWBERY and PHILLIPS), 3048.

$C_{10}H_{10}O_5N_2$ *dl-p*-Nitrobenzoylalanine, resolution of, and its salts (COLLES and GIBSON), 99.

$C_{10}H_{10}O_6N_2$ *2-Nitro-4-acetamidophenoxyacetic acid* (NEWBERY and PHILLIPS), 3049.

$C_{10}H_{11}ON$ 4-Phenyl-2-pyrrolidone (JACKSON and KENNER), 1659.

$C_{10}H_{11}O_2Cl$ Ethyl ω-chloro-*m*-toluate (TITLEY), 2582.

$C_{10}H_{11}O_2Br$ Ethyl ω-bromo-*p*-toluate (TITLEY), 2581.

$C_{10}H_{11}O_5N$ 6-Nitro-3-ethoxy-*p*-toluic acid (CHATTAWAY and CALVET), 1093.
6-Nitro-3-methoxy-4-ethoxybenzaldehyde (BARGER and SILBERSCHMIDT), 2927.

$C_{10}H_{11}O_5N_3$ *2:3-Dinitro-4-acetamidoethylbenzene* (BRADY, DAY, and ALLAM), 951.

$C_{10}H_{11}O_6N$ 5-Nitro-2-ethoxymandelic acid (CHATTAWAY and MORRIS), 3244.

$C_{10}H_{12}O_4Ni$ Methyl ethoxynickelosalicylate (DOAK and PACKER), 2763.

$C_{10}H_{12}O_8N_4$ 2:4:6-Trinitro-5-aminoresorcinol diethyl ether (FLÜRSCHEIM and HOLMES), 3046.

$C_{10}H_{13}OCl$ *p*-Chlorophenyl *iso*butyl ether (BRADFIELD and JONES), 3081.

$C_{10}H_{13}O_2N$ *γ-Amino-β-phenylbutyric acid, and its hydrobromide* (JACKSON and KENNER), 1659.
1-Cyano-2:2:3:3-tetramethyl-[0, 1, 2]-*dicyclo*pentan-4-ol-5-one (INGOLD and SHOPPEE), 368.

$C_{10}H_{13}O_2N_3$ *Aminodiacetylphenylenediamines* (PHILLIPS), 175.

$C_{10}H_{13}O_3N$ β-Amino-α-hydroxydihydro*isosa*frole, and its hydrochloride (READ and REID), 1491.
Nitro-4-methyl benzyl ethyl ethers (INGOLD and ROTHSTEIN), 1279.

$C_{10}H_{13}O_3Br$ Bromo-α-methyl*cyclo*pentane-1:1-diacetic anhydride (BARDHAN), 2598.

$C_{10}H_{14}O_2N_2$ 2-Nitro-4-amino-*tert.*-butylbenzene (SHOESMITH and MACKIE), 2337.

$C_{10}H_{14}O_4Mo$ Molybdyl bisacetylacetone (MORGAN and CASTELL), 3253.

$C_{10}H_{14}NBr$ 2-Bromo-4-amino-*tert.*-butylbenzene, and its hydrochloride (SHOESMITH and MACKIE), 2339.

$C_{10}H_{14}Cl_2Sn$ Phenyl-*n*-butylstannic chloride (KIPPING), 2371.

$C_{10}H_{15}O_2N$ Ethyl *r*-*cyclo*pentylcyanoacetate (VOGEL), 2021.
β-Hydroxy-β-*p*-methoxyphenyl*iso*propylamines, and their salts (READ and REID), 1489.
α-Methyl*cyclo*pentane-diacetimide (BARDHAN), 2598.

$C_{10}H_{15}O_2Br$ Methyl derivative of 1-bromo-2:2:3:3-tetramethyl-[0, 1, 2]-*dicyclo*-

$C_{10}H_{15}O_4S$ *d*-Camphorsulphonic acid, triethylenediaminenickel salt (BUCKNALL and WARDLAW), 2742.

$C_{10}H_{16}O_2Br_2$ Dibromo-5-methoxy-2:2:3:3-tetramethyl*cyclo*pentanone (SHOPPEE), 2363.

$C_{10}H_{17}ON_3$ *cyclo*Hexylideneacetone semicarbazone (DICKINS, HUGH, and KON), 1636.

$C_{10}H_{17}OCl$ Hydroxychlorocarane (PILLAY and SIMONSEN), 364.

$C_{10}H_{17}OAs$ Benzyltrimethylarsonium hydroxide, picrate of (INGOLD, SHAW, and WILSON), 1283.

$C_{10}H_{17}OP$ Benzyltrimethylphosphonium hydroxide, picrate of (INGOLD, SHAW, and WILSON), 1283.

$C_{10}H_{17}O_2N_3$ 3:3:4:4-Tetramethyl*cyclo*pentane-1:2-dione semicarbazone (INGOLD and SHOPPEE), 396.

$C_{10}H_{17}O_3N$ α-Methyl-Δ^1-*cyclo*pentenylacetone semicarbazone (BARDHAN), 2604.
α-Methyl*cyclo*pentylideneacetone semicarbazone (BARDHAN), 2603.

$C_{10}H_{17}O_3N_3$ 1-Acetyl*cyclo*pentane-1-acetic acid semicarbazone (BARDHAN), 2601.
Ethyl *iso*propylideneacetoacetate semicarbazone (JUPP, KON, and LOCKTON), 1642.

$C_{10}H_{19}ON_3$ Tetramethyl*cyclo*pentanone semicarbazones (INGOLD and SHOPPEE), 398.

$C_{10}H_{19}O_3Tl$ Ethyl thallium diethylacetoacetate (MENZIES, SIDGWICK, CUTCLIFFE, and FOX), 1290.

$C_{10}H_{20}Cl_2Te$ 1-ε-Chloroamyl*cyclo*telluripentane 1-chloride (MORGAN and BURGESS), 325.

$C_{10}H_{20}Br_2Te$ 1-ε-Bromoamyl*cyclo*telluripentane 1-bromide (MORGAN and BURGESS), 326.

$C_{10}H_{20}I_2Te$ 1-ε-Iodoamyl*cyclo*telluripentane 1-iodide (MORGAN and BURGESS), 328.

$C_{10}H_{22}O_2S$ Ethyl-*n*-octylsulphone (FENTON and INGOLD), 3129.

10 IV

$C_{10}H_5O_2NCl_4$ 6-Amino-2:4-bisdichloromethylene-1:3-benzdioxin (CHATTAWAY and CALVET), 1091.

$C_{10}H_5O_6N_2Cl_3$ 6:8-Dinitrodichloromethylchloromethylene-1:3-benzdioxin (CHATTAWAY and MORRIS), 3246.

$C_{10}H_6O_4NCl_3$ 6-Nitrodichloromethylchloromethylene-1:3-benzdioxin (CHATTAWAY and MORRIS), 3243.

$C_{10}H_6O_6N_2Cl_4$ 6:8-Dinitro-2:4-bisdichloromethyl-1:3-benzdioxin (CHATTAWAY and MORRIS), 2345.

$C_{10}H_7O_2Cl_4Br$ 6-Bromo-2:4-bisdichloromethyl-1:3-benzdioxin (CHATTAWAY and MORRIS), 3245.

$C_{10}H_7O_2IS$ 1-Iodonaphthalene-2-sulphinic acid (BARBER and SMILES), 1145.

$C_{10}H_7O_3IS$ 1-Iodonaphthalene-2-sulphonic acid (BARBER and SMILES), 1144.

$C_{10}H_7O_4NCl_4$ 6-Nitro-2:4-bisdichloromethyl-1:3-benzdioxin (CHATTAWAY and MORRIS), 3243.

$C_{10}H_7O_4Cl_5S$ 2:4-Bisdichloromethyl-1:3-benzdioxin-6-sulphonyl chloride (CHATTAWAY and MORRIS), 3246.

$C_{10}H_8ON_2Cl_6$ Chloral α-acetyl-2:4:6-trichlorophenylhydrazone (CHATTAWAY and DALDY), 2759.

$C_{10}H_8O_2N_2Cl_4$ Ethyl glyoxylate ω-chloro-2:4:6-trichlorophenylhydrazone (CHATTAWAY and DALDY), 2761.

$C_{10}H_8O_2N_2Br_4$ Ethyl glyoxylate ω-bromo-2:4:6-tribromophenylhydrazone (CHATTAWAY and DALDY), 2762.

$C_{10}H_8O_5Cl_4S$ 2:4-Bisdichloromethyl-1:3-benzdioxin-6-sulphonic acid, and its ammonium salt (CHATTAWAY and MORRIS), 3245.

$C_{10}H_{9}O_{2}NCl_{4}$ 6-Amino-2:4-bisdichloromethyl-1:3-benzdioxin, and its hydrochloride (CHATTAWAY and MORRIS), 3244.

$C_{10}H_{9}O_{2}N_{2}Cl_{3}$ Ethyl glyoxylate 2:4:6-trichlorophenylhydrazone (CHATTAWAY and DALDY), 2759.

$C_{10}H_{9}O_{2}N_{2}Br_{3}$ *Ethylglyoxalate 2:4:6-tribromophenylhydrazone* (CHATTAWAY and DALDY), 2762.

$C_{10}H_{9}O_{3}NI_{2}$ 3:5-Di-iodo-4-acetamidophenyl acetate (HUNTER and BARNES), 2067.

$C_{10}H_{10}ON_{2}S$ 1-Acetamido-3-methylbenzthiazole (HUNTER and STYLES), 3022.
1-Imino-2-acetyl-3-methyl-1:2-dihydrobenzthiazole (HUNTER and STYLES), 3022.

$C_{10}H_{10}O_{2}N_{2}S$ Benziminazolyl-2-α-thiolpropionic acid (STEPHEN and WILSON), 1420.

$C_{10}H_{10}O_{3}NBr$ 5-Bromomethylacetylanthranilic acid (HEILBRON, HOLT, and KITCHEN), 941.

$C_{10}H_{11}ONCl_{2}$ *Acetyldichloro-o-xylidines* (HINKEL, AYLING, and BEVAN), 1877.

$C_{10}H_{11}O_{3}NS$ β-Cyanoethyl toluene-*p*-sulphonate (CLEMO and WATSON), 726.

$C_{10}H_{11}O_{4}N_{2}As$ 3 5-Diacetamido-2-hydroxyphenylarsenoxide (NEWBERY and PHILLIPS), 2378.

$C_{10}H_{11}O_{6}N_{2}As$ Acetamidohydroxy-1:4-benz*iso*oxazine-6-arsinic acid (NEWBERY, PHILLIPS, and STICKINGS), 3058.
8-Acetamido-3-hydroxy-1:4-benz*iso*oxazinearsinic acids (BALABAN), 3069.

$C_{10}H_{12}O_{2}NBr$ 2-Bromo-4-nitro-*tert.*-butylbenzene (SHOESMITH and MACKIE), 2339.

$C_{10}H_{12}O_{5}NAs$ 3-Hydroxy-2-ethyl-1:4-benz*iso*oxazine-6-arsinic acid (NEWBERY, PHILLIPS, and STICKINGS), 3063.

$C_{10}H_{12}O_{6}N_{3}As$ 8-Glycylamino-3-hydroxy-1:4-benz*iso*oxazine-6-arsinic acid (NEWBERY, PHILLIPS, and STICKINGS), 3060.

$C_{10}H_{12}O_{7}NAs$ 2-Acetamidophenoxyacetic acid 4-arsinic acid (NEWBERY, PHILLIPS, and STICKINGS), 3054.

$C_{10}H_{13}ONS$ 2:4-Dimethylthiolacetanilide (HODGSON and HANDLEY), 164.

$C_{10}H_{13}ON_{2}Cl$ Chloroacetamidodimethylanilines (CLEMO and SMITH), 2420.

$C_{10}H_{13}ON_{2}Br$ 4-Bromo-2-acetamidodimethylaniline (CLEMO and SMITH), 2421.

$C_{10}H_{13}O_{5}N_{2}As$ 3:5-Diacetamido-4-hydrophenylarsinous acid (NEWBERY and PHILLIPS), 2376.

$C_{10}H_{13}O_{6}N_{2}As$ 2-Acetamidophenoxyacetamide 4-arsinic acid (NEWBERY, PHILLIPS, and STICKINGS), 3055.
2:4-Diacetamido-3-hydroxyphenylarsinic acid (BALABAN), 812.
3:5-Diacetamido-2-hydroxyphenylarsinic acid (NEWBERY and PHILLIPS), 2376.
8-β-Hydroxyethylamino-3-hydroxy-1:4-benz*iso*oxazine-6-arsinic acid (NEWBERY, PHILLIPS, and STICKINGS), 3062.

$C_{10}H_{13}O_{7}N_{2}As$ 4-ω-Hydroxyacetamido-2-acetamido-3-hydroxyphenylarsinic acid (BALABAN), 3070

$C_{10}H_{16}ONI$ *p*-Dimethylaminobenzyl methiodide (CLEMO and SMITH), 2425.

$C_{10}H_{16}O_{3}NAs$ *p*-Nitrobenzyltrimethylarsonium hydroxide, picrate of (INGOLD, SHAW, and WILSON), 1285.

$C_{10}H_{16}O_{3}NP$ Nitrobenzyltrimethylphosphonium hydroxides, picrates of (INGOLD SHAW, and WILSON), 1284.

10 V

$C_{10}H_{6}O_{2}NCl_{6}Br$ 7-Bromo-6-amino-2:4-bistrichloromethyl-1:3-benzdioxin (CHATTAWAY and CALVET), 1091.

$C_{10}H_{6}O_{2}ClIS$ *1-Iodonaphthalene-2-sulphonyl chloride* (BARBER and SMILES), 1145.

$C_{10}H_{7}O_{2}N_{2}Cl_{4}Br_{3}$ 2:4-Bisdichloromethyl-1:3-benzdioxin-6-diazonium perbromid (CHATTAWAY and MORRIS), 3245.

$C_{10}H_8O_2N_2ClBr_3$ Ethyl glyoxylate ω-chloro-2:4:6-tribromophenylhydrazone (CHATTAWAY and DALDY), 2762.

$C_{10}H_8O_2N_2Cl_3Br$ Ethyl glyoxylate ω-bromo-2:4:6-trichlorophenylhydrazone (CHATTAWAY and DALDY), 2761.

$C_{10}H_9O_3NClBr$ Chlorobromoacetamidophenyl acetates (HUNTER and BARNES), *2060*.

$C_{10}H_9O_3NClI$ Chloroiodoacetamidophenyl acetates (HUNTER and BARNES), 2061.

$C_{10}H_9O_3NBrI$ Bromoiodoacetamidophenyl acetates (HUNTER and BARNES), 2062.

$C_{10}H_9O_4NCl_4S$ 2:4-Bisdichloromethyl-1:3-benzdioxin-6-sulphonamide (CHATTAWAY and MORRIS), 3246.

$C_{10}H_{10}ON_2Br_4S$ 1-Acetamido-3-methylbenzthiazole tetrabromide (HUNTER and STYLES), 3022.

$C_{10}H_{10}ON_2Br_6S$ 1-Acetamido-3-methylbenzthiazole hexabromide (HUNTER and STYLES), 3022.

$C_{10}H_{11}ON_2Br_3S$ *1-Imino-2-acetyl-3-methyl-1:2-dihydrobenzthiazole tribromid* (HUNTER and STYLES), 3022.

C_{11} Group.

$C_{11}H_{10}O_3$ 1-Ketohydrindene-3-acetic acid (JACKSON and KENNER), 577.

$C_{11}H_{10}O_4$ 3:4-Dihydrocoumarin-4-acetic acid (SESHADRI), 169.

$C_{11}H_{10}O_6$ *p*-Carboxybenzylmalonic acid (TITLEY), 2581.

$C_{11}H_{12}O$ 1-Keto-2-methyltetrahydronaphthalene (TITLEY), 2578.

$C_{11}H_{12}O_2$ 4-Hydroxystyryl ethyl ketone (McGOOKIN and SINCLAIR), 1178.

$C_{11}H_{12}O_4$ β-Carboxyphenyl*iso*butyric acids (TITLEY), 2577.
Phenylene-1-acetic-α-propionic acids (TITLEY), 2580.

$C_{11}H_{12}O_5$ 2:5-Dimethoxyphenylpyruvic acid (GULLAND and VIRDEN), 1482.
β-*o*-Hydroxyphenylglutaric acid (SESHADRI), 169.

$C_{11}H_{12}N_2$ 3:4:5:6-Tetrahydro-4-carboline (ASHLEY and ROBINSON), 1376.

$C_{11}H_{13}N$ Tetrahydropentindole (PLANT and RIPPON), 1911.

$C_{11}H_{14}O_2$ *o-tert.*-Butylbenzoic acid (SHOESMITH and MACKIE), 2339.

$C_{11}H_{14}O_3$ 3:4-Dimethoxy-6-ethylbenzaldehyde (BARGER and SILBERSCHMIDT), 2925.
6-Methoxy-3-ethylphenylacetic acid, and its sodium salt (GULLAND and VIRDEN), 931.

$C_{11}H_{14}O_4$ 3:4-Dimethoxy-6-ethylbenzoic acid (BARGER and SILBERSCHMIDT), 2925.
Methyl 5-*cyclo*pentane*spirodicyclo*pentan-4-ol-3-one-1-carboxylate (GOSS), 1309.
ω:3:5-Trimethoxyacetophenone (ROBERTSON, ROBINSON, and SUGIURA), 1535.

$C_{11}H_{14}O_5$ 4-Hydroxy-ω:3:5-trimethoxyacetophenone (BRADLEY and ROBINSON), 1567.
ω-Hydroxy-3:4:5-trimethoxyacetophenone (BRADLEY and ROBINSON), 1551.

$C_{11}H_{14}N_2$ 4-Aminomethyl-1-methyl-3:4-dihydro*iso*quinoline, and its hydrochloride (JACKSON and KENNER), 1659.

$C_{11}H_{16}O_3$ Acetyl derivative of 2:2:3:3-tetramethyl-[0, 1, 2]-*dicyclo*pentan-4-ol-5-one (INGOLD and SHOPPEE), 389.

$C_{11}H_{16}N_2$ α- and β-2:3:7-Trimethyl-1:2:3:4-tetrahydroquinoxalines, resolution of and their salts (GIBSON, NUTLAND, and SIMONSEN), 108.

$C_{11}H_{18}O_3$ 5-Acetoxy-2:2:3:3-tetramethyl*cyclo*pentanone (INGOLD and SHOPPEE), 397.

$C_{11}H_{18}O_4$ β-*cyclo*Hexylglutaric acid, and its silver salt (SIRCAR), 56.

$C_{11}H_{18}N_2$ *αγ-Di(methylamino)-β-*phenylpropane, hydrochloride of (JACKSON and KENNER), 1659.

$C_{11}H_{20}O_2$ Allyl octoate (DEULOFEU), 528.

$C_{11}H_{20}O_6$ Propyl tartrates, rotatory dispersion of (AUSTIN), 1832.

11 III

$C_{11}H_9OBr$ 3-Bromo-2-methoxynaphthalene (CLEMO and SPENCE), 2818.
$C_{11}H_9OI$ 3-Iodo-2-methoxynaphthalene (CLEMO and SPENCE), 2819.
$C_{11}H_9O_6N$ 6-Nitro-3:4-dihydrocoumarin-4-acetic acid, and its disilver salt (SESHADRI), 171
$C_{11}H_{10}O_2Cl_2$ β-Phenylglutaryl chloride (JACKSON and KENNER), 578.
$C_{11}H_{11}ON$ 1:6-Dimethyl-2-quinolone (HAMER), 209.
2-Methoxy-3-naphthylamine (CLEMO and SPENCE), 2818.
$C_{11}H_{11}O_3N$ 7:8-Dimethoxycarbostyril (GULLAND and VIRDEN), 932.
O-Methylindoxylacetic acid (JACKSON and KENNER), 580.
$C_{11}H_{11}O_3Cl$ Ethyl p-chlorobenzoylacetate (BURTON and INGOLD), 920.
$C_{11}H_{11}O_5N$ 5-Nitro-2-ethoxy-p-tolylglyoxylic acid (CHATTAWAY and CALVET), 1093.
$C_{11}H_{11}O_5Cl$ O-Acetylsyringoyl chloride (BRADLEY and ROBINSON), 1551.
$C_{11}H_{11}O_6N$ trans-2-Nitro-3:4-dimethoxycinnamic acid (GULLAND and VIRDEN), 932.
$C_{11}H_{11}NI_2$ 2-Iodo-6-methylquinoline methiodide (HAMER), 210.
2-Iodoquinoline ethiodide (HAMER), 209.
$C_{11}H_{12}O_2N_2$ 1-2-Pyrrolidone-5-carboxyanilide (GRAY), 1265.
$C_{11}H_{13}O_4N$ 2-Amino-3:4-dimethoxycinnamic acid, and its hydrochloride (GULLAND and VIRDEN), 932.
$C_{11}H_{13}O_5N$ Methylopianic oximes (BRADY, BAKER, GOLDSTEIN, and HARRIS), 536.
$C_{11}H_{13}O_6N$ Dimethyl hydrogen 3-amino-1-methyldicyclopentene-2:4:5-tricarboxylate (GOSS and INGOLD), 1275.
5-Nitro-2-ethoxy-4-methylmandelic acid (CHATTAWAY and CALVET), 1093.
$C_{11}H_{13}N_2I$ Dimethylquinoxaline methiodide (BENNETT and WILLIS), 1975.
$C_{11}H_{14}N_2S$ 1-n-Propylamino-3-methylbenzthiazole (HUNTER and STYLES), 3026.
$C_{11}H_{15}ON$ γ-Imino-γ-ethoxy-α-phenylpropane, hydrochloride of (CLEMO and WATSON), 728.
$C_{11}H_{15}O_2N_3$ 6-Methoxy-3-ethylbenzaldehyde semicarbazone (GULLAND and VIRDEN), 930.
$C_{11}H_{15}O_3Cl$ Acetyl derivative of 1-chloro-2:2:3:3-tetramethyl-[0, 1, 2]-dicyclopentan-4-ol-5-one (INGOLD and SHOPPEE), 408.
$C_{11}H_{16}O_2N_4$ β-Phenylglutardihydrazide (JACKSON and KENNER), 1658.
$C_{11}H_{16}O_4N_4$ 3-Methyl-5-pyrazolone-1-carboxy-α-carbethoxyisopropylidenehydrazide (MUNRO and WILSON), 1260.
$C_{11}H_{16}N_2S$ s-o-Tolyl-n-propylthiocarbamide (HUNTER and STYLES), 3026.
$C_{11}H_{17}O_2N$ Ethyl r-cyclohexylcyanoacetate (VOGEL), 2028.
$C_{11}H_{17}O_3N_3$ Δ^1-cycloHexenylacetoacetic acid semicarbazone (JUPP, KON, and LOCKTON), 1640.
$C_{11}H_{17}O_5Br$ Ethyl α-bromo-α-acetylglutarate (CLEMO and WELCH), 2626.
$C_{11}H_{19}ON_3$ l-Carene oxide semicarbazone (PILLAY and SIMONSEN), 863.
$C_{11}H_{19}O_3N$ 5-Acetoxy-2:2:3:3-tetramethylcyclopentaneoxime (INGOLD and SHOPPEE), 1871.
$C_{11}H_{19}O_3N_3$ Methyl 1-acetylcyclopentane-1-acetate semicarbazone (BARDHAN), 2601.
$C_{11}H_{19}O_4N$ Ethyl α-(α′-aminoethylidene)glutarate (CLEMO and WILSON), 2627.
$C_{11}H_{20}O_2N_2$ β-cycloHexylglutardiamide (SIRCAR), 56.
$C_{11}H_{21}ON$ Acetyltetramethylcyclopentylamines (INGOLD and SHOPPEE), 394, 399; (SHOPPEE), 1670.

11 IV

$C_{11}H_7O_4NCl_6$ 6-Nitro-7-methyl-2:4-bistrichloromethyl-1:3-benzdioxin (CHATT-

$C_{11}H_7O_8N_4Cl$ Ethyl 2:4-trinitrophenylchlorocyanoacetate (FAIRBOURNE and FAWSON), 1080.

$C_{11}H_{10}O_5Cl_4S$ Methyl 2:4-bisdichloromethyl-1:3-*benzdioxin-6-sulphonate* (CHATTAWAY and MORRIS), 3246.

$C_{11}H_{10}O_7N_3Cl$ Ethyl 2:4-dinitrophenylchloromalonamate (FAIRBOURNE and FAWSON), 1078.

$C_{11}H_{11}O_2N_2Br$ 1-2-Pyrrolidone-5-carboxy-*p*-bromoanilide (GRAY), 1266.

$C_{11}H_{12}ON_2S$ Acetyl derivative of 1-methylamino-3-methylbenzthiazole (HUNTER and STYLES), 3025.

$C_{11}H_{12}O_2N_2S$ Benziminazolyl-2-*a*-thiol-*n*-butyric acid (STEPHEN and WILSON), 1419.

$C_{11}H_{12}O_3NCl$ Diacetyl derivative of 3-chloro-2-aminoanisole (HODGSON and KERSHAW), 192.

$C_{11}H_{13}O_3NHg$ 3-Acetoxymercuriaceto-*p*-toluidide (BELL), 2778.

$C_{11}H_{13}N_2BrS$ 5-Bromo-1-*n*-propylamino-3-methylbenzthiazole (HUNTER and STYLES), 3026.

$C_{11}H_{14}N_2Br_2S$ 5-Bromo-1-*n*-propylamino-3-methyl*benzthiazole hydrobromide* (HUNTER and STYLES), 3026.

$C_{11}H_{14}N_2Br_4S$ 1-*n*-Propylamino-3-methylbenzthiazole tetrabromide (HUNTER and STYLES), 3026.

$C_{11}H_{15}O_2NS_3$ *β*-Dithian monoxide *S*-*p*-toluenesulphonylimine (BELL and BENNETT), 92.

$C_{11}H_{15}N_2BrS$ *s*-5-Bromo-*o*-tolyl-*n*-propylthiocarbamide (HUNTER and STYLES), 3026.

1-*n*-Propylamino-3-methylbenzthiazole hydrobromide (HUNTER and STYLES), 3026.

$C_{11}H_{17}NCl_2As$ *l*-*a*-Phenylethylaminopropyldichloroarsine hydrochloride (GOUGH and KING), 2443.

$C_{11}H_{22}O_4NAs$ *γ*-3-Carbethoxypiperidinopropylarsinic acid (GOUGH and KING), 2446.

$C_{11}H_{24}O_3NAs$ *γ*-2:2:6-Trimethylpiperidinopropylarsinic acid (GOUGH and KING), 2445.

$C_{11}H_{24}O_4NAs$ *γ*-4-Hydroxy-2:2:6-trimethylpiperidinopropylarsinic acid (GOUGH and KING), 2444.

11 V

$C_{11}H_{14}O_7N_2ClAs$ 3-*ω*-Chlorocarbethoxyamino-5-acetamido-4-hydroxyphenylarsinic acid (NEWBERY, PHILLIPS, and STICKINGS), 3064.

C_{12} Group.

$C_{12}H_7Cl_3$ Trichlorodiphenyls (HINKEL and HEY), 2791.

$C_{12}H_8S_2$ Diphenylene 2:2′-disulphide (BARBER and SMILES), 1146.

$C_{12}H_{10}O_2$ 2-Phenyl-6-methyl-4-pyrone, and its salts (GIBSON and SIMONSEN), 2307.

$C_{12}H_{10}O_3$ Methoxynaphthoic acids (BRETSCHER, RULE, and SPENCE), 1500.

$C_{12}H_{10}Cl_2$ 3:5-Dichloro-1-phenyl-$\Delta^{2:4}$-*cyclo*hexadiene (HINKEL and HEY), 2789.

$C_{12}H_{10}S_2$ 2:2′-Dithioldiphenyl (BARBER and SMILES), 1146.

$C_{12}H_{12}O_3$ Methyl 1-ketohydrindene-3-acetate (JACKSON and KENNER), 578.

$C_{12}H_{12}O_4$ *β*-*p*-Methoxyphenylglutaric anhydride (JACKSON and KENNER), 1660.

7-Methyl-3:4-dihydrocoumarin-4-acetic acid (SESHADRI), 170.

$C_{12}H_{12}O_5$ 3:4-Dimethoxy-*a*-methylhomophthalic anhydride (KOEPFLI and PERKIN), 2898.

$C_{12}H_{12}O_6$ Diacetylgallacetophenone (PERKIN and STOREY), 242.

3:4-Dimethoxybenzylidenemalonic acid (JACKSON and KENNER),

$C_{12}H_{12}S_2$ 1:8-Dimethyldithiolnaphthalene (PRICE and SMILES), 2

$C_{12}H_{14}O_2$ Hydroxystyryl propyl ketones (McGookin and Sinclair), 1175.
$C_{12}H_{14}O_3$ 5:6-Dimethoxy-3-methyl-1-hydrindone (Koepfli and Perkin), 2996.
Methoxystyryl ethyl ketones, hydroxy- (McGookin and Sinclair), 1174.
$C_{12}H_{14}O_4$ γ-o-Carboxyphenyl-α-methylbutyric acid (Titley), 2578.
6-Methoxy-3-ethylphenylpyruvic acid, and its sodium salt (Gulland and Virden), 930.
Methyl carboxyphenylpropionates (Titley), 2581.
Methyl phenylenediacetates (Titley), 2579.
β-Veratrylcrotonic acid (Koepfli and Perkin), 2996.
$C_{12}H_{14}O_5$ β-p-Methoxyphenylglutaric acid (Jackson and Kenner), 1660.
β-p-Methyl-o-hydroxyphenylglutaric acid (Seshadri), 170.
$C_{12}H_{14}O_7$ Methyl 5-methyl*dicyclo*penten-3-ol-1:2:4-tricarboxylate (Goss and Ingold), 1272.
$C_{12}H_{15}N$ Hexahydroquinidenes (Perkin and Plant), 644.
8-Methyltetrahydropentindole, and its salts (Plant and Rippon), 1912.
$C_{12}H_{16}O_3$ Butyl *l*-mandelates, rotatory dispersion of (Wood, Chrisman, an Nicholas), 2180.
$C_{12}H_{16}O_4$ 3:4-Dimethoxy-6-ethylphenylacetic acid (Barger and Silberschmidt) 2926.
β-Veratrylbutyric acid (Koepfli and Perkin), 2996.
$C_{12}H_{18}O_2$ *cyclo*Hexane*spiro*-4-methyl*cyclo*hexane-3:5-dione (Dickins, Hugh, an Kon), 1636.
$C_{12}H_{18}O_4$ Ethyl ester of α-hydroxy-α-methyl*cyclo*pentane-1:1-diacetolactor (Bardhan), 2598.
$C_{12}H_{18}O_7$ α-Phenylglucoside hydrate (Hickinbottom), 3147.
$C_{12}H_{18}O_8$ Ethyl diacetyltartrate (Findlay and Campbell), 1772.
Methyl dipropionyl tartrate (Findlay and Campbell), 1773.
$C_{12}H_{20}O_4$ Ethyl 1-carboxy*cyclo*pentane-1-acetate (Vogel), 2022.
$C_{12}H_{20}O_5$ Ethyl α-*iso*propylacetonedicarboxylate (Hariharan, Menon, an Simonsen), 435.
$C_{12}H_{22}O_5$ Ethyl β-hydroxy-α-*iso*propylglutarate (Hariharan, Menon, and Simonsen), 436.
$C_{12}H_{22}O_6$ Butyl tartrates, rotatory dispersion of (Austin), 1833.
$C_{12}H_{22}O_8$ Irigenin trimethyl ether (Baker), 1028.
$C_{12}H_{24}O_2$ Lauric acid, potassium salt, hydrolysis in solutions of (McBain a Eaton), 2166.
$C_{12}H_{24}O_3$ 11-Hydroxydodecoic acid, and its magnesium salt (Bhattachar Salknone, and Simonsen), 2679.
$C_{12}H_{26}N_2$ Tetraethylpiperazine, salts of (Gough and King), 2433.

12 III

$C_{12}H_6O_4Cl_6$ 5:7-Dichloro-6-acetoxy-2:4-bistrichloromethyl-1:3-benzdioxin (Chaaway and Calvet), 2918.
$C_{12}H_7N_2Cl$ 2-Chlorophenazine (McCombie, Scarborough, and Waters), 356.
$C_{12}H_7N_2Br$ 2-Bromophenazine (McCombie, Scarborough, and Waters), 356
$C_{12}H_8OBr_2$ 4:5-Dibromo-3-hydroxydiphenyl (Hinkel and Hey), 1203.
$C_{12}H_8OS$ Phenoxthionine (Drew), 519.
$C_{12}H_8OSe$ Phenoxselenine (Drew), 521.
$C_{12}H_8OTe$ Phenoxtellurine, determination of, in tellurylium compounds (Dr 509.
$C_{12}H_8O_2S$ Phenoxthionine oxide (Drew), 520.
$C_{12}H_8O_2Se$ Phenoxselenine oxide (Drew), 522.
$C_{12}H_8O_2S_2$ Diphenylene 2:2′-disulphoxide (Barber and Smiles), 114

$C_{12}H_8O_3S$ Phenoxthionine dioxide (DREW), 520.
$C_{12}H_8O_6N_4$ 3:5:4′-Trinitro-2-aminodiphenyl (BELL), 2775.
$C_{12}H_8N_2Cl_2$ 4:4′-Dichloroazobenzene (BURNS, MCCOMBIE, and SCARBOROUGH), 2933.
$C_{12}H_8N_2Br_2$ 3:5-Dibromoazobenzene (BURNS, MCCOMBIE, and SCARBOROUGH), 2936.
$C_{12}H_8I_2S_2$ Di-2-iodophenyl disulphide (BARBER and SMILES), 1144.
$C_{12}H_9OBr$ 5-Bromo-3-hydroxydiphenyl (HINKEL and HEY), 1203.
$C_{12}H_9O_4N$ 3:4-Dihydrocoumarin-4-cyanoacetic acid (SESHADRI), 169.
$C_{12}H_9O_4N_3$ Dinitroaminodiphenyls (BELL), 2774.
Ethyl *n*-nitrophenyldicyanoacetate (FLÜRSCHEIM and HOLMES), 2240.
$C_{12}H_9O_5N_3$ 6-Nitro-3:4-dihydrocoumarin-4-cyanoacetamide (SESHADRI), 170.
$C_{12}H_9NCl_2$ Dichloroaminodiphenyls (HINKEL and HEY), 2790.
$C_{12}H_9N_3Br_2$ 3:5-Dibromo-4-aminoazobenzene (BURNS, MCCOMBIE, and SCARBOROUGH), 2935.
$C_{12}H_{10}O_2N_2$ Ethyl phenyldicyanoacetate (FLÜRSCHEIM and HOLMES), 2237.
5-Nitro-2-aminodiphenyl (BELL), 2774.
$C_{12}H_{10}O_2S$ Diphenylsulphone, parachor for (FREIMAN and SUGDEN), 268.
$C_{12}H_{10}O_3N_2$ 3:4-Dihydrocoumarin-4-cyanoacetamide (SESHADRI), 168.
$C_{12}H_{10}O_3Se$ Phenoxselenine dihydroxide (DREW), 522.
$C_{12}H_{10}O_4S_2$ Diphenyl-4:4′-disulphinic acid (BARBER and SMILES), 1148.
$C_{12}H_{10}O_5N_2$ ω-Diazo-3:4-diacetoxyacetophenone (BRADLEY and SCHWARZENBACH), 2907.
$C_{12}H_{10}NBr$ 5-Bromo-3-aminodiphenyl (HINKEL and HEY), 1839.
$C_{12}H_{10}N_2Br_2$ 2:6-Dibromobenzidine (BURNS, MCCOMBIE, and SCARBOROUGH), 2936.
5:4′-Dibromo-3:4-diaminodiphenyl (HINKEL and HEY), 1840.
3:5-Dibromohydrazobenzene (BURNS, MCCOMBIE, and SCARBOROUGH), 2936.
$C_{12}H_{10}N_3Cl$ 3-Chloro-4-aminoazobenzene (BURNS, MCCOMBIE, and SCARBOROUGH), 2935.
$C_{12}H_{11}OBr$ 5-Bromo-1-phenyl-Δ^4-*cyclo*hexen-3-one (HINKEL and HEY), 1202.
$C_{12}H_{11}OBr_3$ 4:5:5-Tribromo-1-phenyl*cyclo*hexan-3-one (HINKEL and HEY), 1202.
$C_{12}H_{11}O_2N_3$ 3-Nitrobenzidine (LE FÈVRE and TURNER), 253.
$C_{12}H_{11}O_3N_3$ 6-Amino-3:4-dihydrocoumarin-4-cyanoacetamide (SESHADRI), 171.
$C_{12}H_{11}O_4N$ *iso*Nitroso-derivative of methyl 1-ketohydrindene-3-acetate (JACKSON and KENNER), 578.
$C_{12}H_{11}O_5Br$ 6-Bromo-3:4-dimethoxy-α-methylhomophthalic anhydride (KOEPFLI and PERKIN), 2993.
$C_{12}H_{11}O_5Cl$ ω-Chloro-3:4-diacetoxyacetophenone (BRADLEY and SCHWARZENBACH), 2908.
$C_{12}H_{11}NAs_2$ 4-Aminoarsenobenzene, and its hydrochloride (NEWBERY and PHILLIPS), 120.
$C_{12}H_{11}NSe$ 4-Aminodiphenyl selenide, and its hydrochloride (GAYTHWAITE, KENYON, and PHILLIPS), 2290.
$C_{12}H_{11}N_2Cl$ 2-Chlorobenzidine (BURNS, MCCOMBIE, and SCARBOROUGH), 2935.
$C_{12}H_{11}N_2Br$ 4′-Bromo-2-aminodiphenylamine (MCCOMBIE, SCARBOROUGH, and WATERS), 356.
$C_{12}H_{12}O_5N_2$ 6-Amino-3:4-dihydrocoumarin-4-carbamylacetic acid, and its hydrochloride (SESHADRI), 172.
$C_{12}H_{13}O_2N$ Acetyl derivative of 4-phenyl-2-pyrrolidone (JACKSON and KENNER), 1659.
$C_{12}H_{13}O_3N_3$ 1-Ketohydrindene-3-acetic acid semicarbazone (JACKSON and KENNER), 578.

$C_{12}H_{13}O_3Br$ 4-Bromo-6:7-dimethoxy-3-methyl-1-hydrindone (KOEPFLI and PERKIN) 2997.

$C_{12}H_{13}O_4N$ *iso*Nitroso-5:6-dimethoxy-3-methyl-1-hydrindone (KOEPFLI and PERKIN), 2997.

$C_{12}H_{14}O_3N_2$ γδ-Diketohexoic acid γ-phenylhydrazone (CLEMO and WELCH), 2627.

$C_{12}H_{14}O_5N_2$ Ethyl *p*-nitrobenzoylalanines (COLLES and GIBSON), 107.

$C_{12}H_{15}ON$ Δα-Hexenanilide (GOLDBERG and LINSTEAD), 2351.

Methylpentenoic anilides (GOLDBERG and LINSTEAD), 2353.

$C_{12}H_{15}O_2Tl$ Thallium dimethyl benzoylacetone (MENZIES, SIDGWICK, CUTCLIFFE, and FOX), 1290.

$C_{12}H_{15}O_3N$ 5:6-Dimethoxy-3-methyl-1-hydrindone oxime (KOEPFLI and PERKIN), 2997.

$C_{12}H_{15}O_3Cl_9$ Parabutylchlorals (CHATTAWAY and KELLETT), 2712.

$C_{12}H_{15}O_4Br$ 6-Bromo-β-veratrylbutyric acid (KOEPFLI and PERKIN), 2997.

$C_{12}H_{15}O_6N$ Methyl 3-amino-1-methyl*dicyclo*pentene-2:4:5-tricarboxylate (GOSS and INGOLD), 1274.

Methyl 3-methyl-1:2-dicarbomethoxy*cyclo*propane-3-cyanoacetate (GOSS and INGOLD), 1273.

$C_{12}H_{16}O_5S$ β-Carbethoxyethyl toluene-*p*-sulphonate (CLEMO and WATSON), 727.

$C_{12}H_{17}O_2N$ Ethyl *cyclo*heptylidenecyanoacetate (VOGEL), 2024.

$C_{12}H_{17}O_2N_3$ Aldehydomethyl*iso*propylphenol semicarbazones (BELL and HENRY), 2219, 2221.

$C_{12}H_{17}O_4N_3$ ω:3:5-Trimethoxyacetophenone semicarbazone (ROBERTSON, ROBINSON, and SUGUIRA), 1536.

$C_{12}H_{18}O_2N_6$ Thymoquinone disemicarbazone (HENRY and PAGET), 80.

$C_{12}H_{18}O_3N_4$ β-*p*-Methoxyphenylglutaric dihydrazide (JACKSON and KENNER), 1660.

$C_{12}H_{18}O_6Mo$ Molybdyl bispropionylacetone (MORGAN and CASTELL), 3254.

$C_{12}H_{19}O_2N$ Ethyl *r*-*cyclo*heptylcyanoacetate (VOGEL), 2025.

$C_{12}H_{21}O_4Cl$ Ethyl β-chloro-α-*iso*propylglutarate (HARIHARAN, MENON, and SIMONSEN), 436.

12 IV

$C_{12}H_6O_2NCl_3$ 2:3:5-Trichloro-4′-nitrodiphenyl (HINKEL and HEY), 2791.

$C_{12}H_6O_2N_2Cl_4$ Tetrachlorodihydroxyazobenzenes (HUNTER and BARNES), 2054.

$C_{12}H_6O_2N_2I_4$ 3:5:3′:5-Tetraiodo-2:2′-dihydroxyazobenzene (HUNTER and BARNES), 2058.

$C_{12}H_6O_4Cl_4S_2$ 4:4′-Dichlorodiphenyl-3:3′-disulphonyl chloride (BARBER and SMILES), 1147.

$C_{12}H_7O_2NCl_2$ Dichloronitrodiphenyls (HINKEL and HEY), 2790.

$C_{12}H_7O_2NBr_2$ 4:5-Dibromo-3-nitrodiphenyl (HINKEL and HEY), 1839.

$C_{12}H_7O_2N_2Cl_3$ Trichlorodihydroxyazobenzenes (HUNTER and BARNES), 2053.

$C_{12}H_7O_3NCl_4$ 6-Acetylamino-2:4-bisdichloromethylene-1:3-benzdioxin (CHATTAWAY and CALVET), 1091.

$C_{12}H_8ON_2Cl_2$ 4:4′-Dichloroazoxybenzene (BURNS, MCCOMBIE, and SCARBOROUGH), 2933.

3:5-Dichloro-4-hydroxyazobenzene (BURNS, MCCOMBIE, and SCARBOROUGH), 2934.

$C_{12}H_8ON_2I_2$ 3:5-Di-iodo-4-hydroxyazobenzene (HUNTER and BARNES), 2067.

$C_{12}H_8O_2N_2Cl_2$ Dichlorodihydroxyazobenzenes (HUNTER and BARNES), 2058.

$C_{12}H_8O_2N_2Br_2$ Dibromodihydroxyazobenzenes (HUNTER and BARNES), 2052.

$C_{12}H_8O_2N_2I_2$ 5:5′-Di-iodo-2:2′-dihydroxyazobenzene (HUNTER and BARNES), 2067.

$_{12}H_8O_3N_3Cl$ Chloronitroazobenzenes (BURNS, MCCOMBIE, and SCARBOROUGH), 2983.

$_{12}H_8O_7N_2S$ Nitrophenyl *p*-nitrobenzenesulphonates (BELL), 2777.

$_{12}H_9ON_2Br$ 3-Bromo-4-hydroxyazobenzene, and its hydrochloride (HUNTER and BARNES), 2064.

$_{12}H_9ON_2I$ 3-Iodo-4-hydroxyazobenzene, and its hydrochloride (HUNTER and BARNES), 2064.

$_{12}H_9O_2N_2Cl$ Chlorodihydroxyazobenzenes (HUNTER and BARNES), 2053.

$_{12}H_9O_2N_2Br$ Bromodihydroxyazobenzenes (HUNTER and BARNES), 2054.

4′-Bromo-2-nitrodiphenylamine (MCCOMBIE, SCARBOROUGH, and WATERS), 856.

$_{12}H_9O_2N_2I$ 5-Iodo-2:2′-dihydroxyazobenzene (HUNTER and BARNES), 2057.

$_{12}H_9O_5NS$ Phenyl *p*-nitrobenzenesulphonate (BELL), 2777.

$_{12}H_{11}ONSe$ 4-Aminodiphenyl selenoxide (GAYTHWAITE, KENYON, and PHILLIPS), 2291.

$_{12}H_{11}OClBr_2$ 5-Chloro-4:5-dibromo-1-phenyl*cyclo*hexan-3-one (HINKEL and HEY), 1204.

$_{12}H_{11}O_2N_2Cl$ 6-Chloronitrotetrahydrocarbazoles (PLANT and ROSSER), 2462.

$_{12}H_{11}O_3NCl_4$ 6-Acetamido-2:4-bisdichloromethyl-1:3-benzdioxin (CHATTAWAY and MORRIS), 3244.

$_{12}H_{11}O_3N_2Cl_3$ Ethyl glyoxylate *a*-acetyl-2:4:6-trichlorophenylhydrazone (CHATTAWAY and DALDY), 2760.

Ethyl 2:4:6-trichlorobenzeneazoacetoacetate (CHATTAWAY and DALDY), 2761.

$_{12}H_{11}O_3N_2Br_3$ Ethyl glyoxylate *a*-acetyl-2:4:6-tribromophenylhydrazone (CHATTAWAY and DALDY), 2762.

Ethyl 2:4:6-tribromobenzeneazoacetoacetate (CHATTAWAY and DALDY), 2762.

$_{12}H_{12}O_2N_2As_2$ 3:4′-Diamino-4:3′-dihydroxyarsenobenzene (BALABAN), 811.

$_{12}H_{12}O_3NAs$ Diphenylamine-*p*-arsinic acid, and its hydrochloride (GIBSON and JOHNSON), 1286.

$_{12}H_{12}O_3N_2S$ Ethyl 4-keto-3:4-dihydroquinazoline-2-thioglycollate (STEPHEN and WILSON), 1421.

$_{12}H_{12}O_4NBr$ 4-Bromo-2-*iso*nitroso-6:7-dimethoxy-3-methyl-1-hydrindone (KOEPFLI and PERKIN), 2997.

$_{12}H_{12}O_5Cl_4S$ Ethyl 2:4-bisdichloromethyl-1:3-benzdioxin-6-sulphonate (CHATTAWAY and MORRIS), 3246.

$_{12}H_{14}O_2N_2S$ Ethyl benziminazolyl-2-α-thiolpropionate (STEPHEN and WILSON), 1419.

$_{12}H_{14}O_2N_3Cl$ *cyclo*Hexanone chloronitrophenylhydrazones (PLANT and ROSSER), 2461.

$_{12}H_{14}O_4NBr$ 4-Bromo-6:7-dimethoxy-3-methyl-1-hydrindone oxime (KOEPFLI and PERKIN), 2997.

$_{12}H_{15}O_6N_2As$ 8-Acetamido-3-hydroxy-2-ethyl-1:4-benz*iso*oxazine-6-arsinic acid (NEWBERY, PHILLIPS, and STICKINGS), 3063.

$_{12}H_{17}O_4NS$ γ-Imino-γ-ethoxypropyl toluene-*p*-sulphonate, hydrochloride of (CLEMO and WATSON), 727.

$_{12}H_{26}O_5NAs$ γ-Carbethoxy-*n*-hexylaminopropylarsinic acid (GOUGH and KING), 2443.

12 V

$_{12}H_6O_2N_2Cl_2Br_2$ Dichlorodibromodihydroxyazobenzenes (HUNTER and BARNES), 2060.

$_{12}H_6O_2N_2Cl_2I_2$ Dichlorodi-iododihydroxybenzenes (HUNTER and BARNES), 2061.

$_{12}H_6O_2N_2Br_2I_2$ Dibromodi-iododihydroxybenzenes (HUNTER and BARNES), 2062.

$_{12}H_8ON_2ClBr$ 3-Chloro-5-bromo-4-hydroxyazobenzene (HUNTER and BARNES), [illegible]

$C_{12}H_8ON_2ClI$ 3-Chloro-5-iodo-4-hydroxyazobenzene (HUNTER and BARNES), 2065.
$C_{12}H_8ON_2BrI$ 3-Bromo-5-iodo-4-hydroxyazobenzene (HUNTER and BARNES), 2066.
$C_{12}H_8O_3NCl_6Br$ 7-Bromo-6-acetylamino-2:4-bistrichloromethyl-1:3-benzdioxin (CHATTAWAY and CALVET), 1091.

C_{13} Group.

$C_{13}H_{10}N_2$ 1-Methylphenazine, and its chloroplatinate (MCCOMBIE, SCARBOROUGH, and WATERS), 356.
$C_{13}H_{11}O$ Phenyl benzyl ether, rearrangement of (SHORT), 528.
$C_{13}H_{12}O_3$ Methyl 8-methoxy-1-naphthoate (BRETSCHER, RULE, and SPENCE), 1500.
$C_{13}H_{12}Se$ Phenyl *p*-tolyl selenide (GAYTHWAITE, KENYON, and PHILLIPS), 2283.
$C_{13}H_{13}N$ *Benzylaniline, nitration of* (*REILLY, MOORE, and DRUMM*), *563.*
$C_{13}H_{14}O_3$ Ethyl 1-ketohydrindene-3-acetate (JACKSON and KENNER), 578.
Ethyl 2-methyl-1-hydrindone-2-carboxylate (TITLEY), 2577.
$C_{13}H_{14}O_5$ 3:3′-Dimethoxydiphenylglutaric anhydride (JACKSON and KENNER), 1661.
$C_{13}H_{14}O_6$ *2:4-Diacetylgallacetophenone 3-methyl ether* (*PERKIN and STOREY*), *242.*
$C_{13}H_{14}N_2$ *2-Amino-2′-methyldiphenylamine, and its tin salt* (*MCCOMBIE*, SCARBOROUGH, and WATERS), 355.
Propane-*αγ*-dipyridine, salts of (GOUGH and KING), 2447.
$C_{13}H_{15}N$ 3-Methyltetrahydrocarbazole (PLANT and ROSSER), 2457.
2:3:4:5-Tetrahydroheptindole, and its picrate (PERKIN and PLANT), 2586.
$C_{13}H_{16}O_2$ 2-Hydroxystyryl *tert.*-butyl ketone (MCGOOKIN and SINCLAIR), 1176.
$C_{13}H_{16}O_3$ Hydroxymethoxystyryl propyl ketones (MCGOOKIN and SINCLAIR), 1174.
$C_{13}H_{16}O_4$ 2-Hydroxystyryl *iso*butenyl ketone (MCGOOKIN and SINCLAIR), 1176.
$C_{13}H_{16}O_6$ 3:3′-Dimethoxydiphenylglutaric acid (JACKSON and KENNER), 1661.
Ethyl syringoylacetate (BRADLEY and ROBINSON), 1554.
$C_{13}H_{17}N$ Hexahydroheptindole, and its salts (PERKIN and PLANT), 2586.
3-Methylhexahydrocarbazoles (*PLANT and ROSSER*), *2460.*
$C_{13}H_{20}O$ Substance, from piperitone and ethyl acetoacetate (JUPP, KON, and LOCKTON), 1644.
$C_{13}H_{20}O_4$ *trans*-Decahydro-*β*-naphthylmalonic acid (VOGEL), 2027.
$C_{13}H_{22}O$ Luparone (CHAPMAN), 1303.
$C_{13}H_{22}O_4$ *Methyl β-cyclohexylglutarate* (*SIRCAR*), *56.*
$C_{13}H_{22}N_2$ Base, and its salts, from lupanine methiodide and caustic potash (*CLEMO and LEITCH*), *1818.*
$C_{13}H_{24}O_4$ Methyl hydrogen decane-1:10-dicarboxylate (BHATTACHARYA, SALETORE, and SIMONSEN), 2679.

13 III

$C_{13}H_4O_{10}N_4$ 2:4:5:7-Tetranitroxanthrone (LE FÈVRE), 3251.
$C_{13}H_5O_7N_3$ 2:4:7-Trinitrofluorenone (BELL), 1990.
$C_{13}H_6O_5S$ Thioxanthone dioxide 1:4-quinone (PRICE and SMILES), 3158.
$C_{13}H_8OS_2$ Diphenylene 2:2′-dithiolcarbonate (BARBER and SMILES), 1146.
$C_{13}H_8O_4S$ *2-Hydroxythioxanthone dioxide* (*PRICE and SMILES*), *3158.*
$C_{13}H_8O_5S$ Dihydroxythioxanthone dioxides (PRICE and SMILES), 3158.
$C_{13}H_9O_2N$ Carbazole-1-carboxylic acid (BRISCOE and PLANT), 1990.
$C_{13}H_9O_2N_3$ 1-Benzoyloxy-1:2:3-benztriazole (BRADY and REYNOLDS), 197.

$C_{13}H_9N_2Br_3$ Substance, from 2-methylazobenzene and bromine (BURNS, MCCOMBIE, and SCARBOROUGH), 2932.

$C_{13}H_{10}ON_2$ 2-Methoxyphenazine, and its chloroplatinate (MCCOMBIE, SCARBOROUGH, and WATERS), 358.

$C_{13}H_{10}O_2N_2$ Benzylidene-*m*-nitroaniline, hydrochloride of (FLÜRSCHEIM and HOLMES), 2241.

$C_{13}H_{10}O_2Se$ 4-Carboxydiphenyl selenide (GAYTHWAITE, KENYON, and PHILLIPS), 2285.

$C_{13}H_{10}O_3S$ 2-Carboxy-4′-hydroxydiphenyl sulphide (PRICE and SMILES), 2862.

$C_{13}H_{10}O_3Se$ 4-Carboxydiphenyl selenoxide, and its salts (GAYTHWAITE, KENYON, and PHILLIPS), 2284.

$C_{13}H_{10}O_4N_4$ Dinitromethylazobenzenes (BURNS, MCCOMBIE, and SCARBOROUGH), 2932.

$C_{13}H_{10}O_4S$ 2-Carboxy-2′:4′-dihydroxydiphenyl sulphide (PRICE and SMILES), 2862.

$C_{13}H_{10}O_5N_4$ 3:4′-Dinitro-4-methoxyazobenzene (BURNS, MCCOMBIE, and SCARBOROUGH), 2935.

$C_{13}H_{10}O_5S$ 2:4-Dihydroxy-2′-carboxydiphenyl sulphoxide (PRICE and SMILES), 3157.

$C_{13}H_{10}O_6S$ 2:5-Dihydroxydiphenylsulphone-2′-carboxylic acid (PRICE and SMILES), 3156.

$C_{13}H_{11}O_2N_3$ Nitromethylazobenzenes (BURNS, MCCOMBIE, and SCARBOROUGH), 2931.

$C_{13}H_{11}O_4N$ 7-Methyl-3:4-dihydrocoumarin-4-cyanoacetic acid (SESHADRI), 170.

$C_{13}H_{11}NS$ Thiobenzanilide, thermal decomposition of (CHAPMAN), 1894.

$C_{13}H_{11}N_2Br$ Bromomethylazobenzenes (BURNS, MCCOMBIE, and SCARBOROUGH), 2931.

$C_{13}H_{12}OSe$ Phenyl *p*-tolyl selenoxide (GAYTHWAITE, KENYON, and PHILLIPS), 2284.

$C_{13}H_{12}O_2N_2$ 2-Aminodiphenylamine-2′-carboxylic acid, and its hydrochloride (MCCOMBIE, SCARBOROUGH, and WATERS), 358.
2-Nitro-2′-methyldiphenylamine (MCCOMBIE, SCARBOROUGH, and WATERS), 355.

$C_{13}H_{12}O_2S$ Phenylbenzylsulphone, parachor for (FREIMAN and SUGDEN), 268.

$C_{13}H_{12}O_3N_2$ 7-Methyl-3:4-dihydrocoumarin-4-cyanoacetamide (SESHADRI), 170.
2-Nitromethoxydiphenylamines (MCCOMBIE, SCARBOROUGH, and WATERS), 357.

$C_{13}H_{12}SeBr_2$ Phenyl *p*-tolyl selenide dibromide (GAYTHWAITE, KENYON, and PHILLIPS), 2283.

$C_{13}H_{12}SnCl_2$ *Phenylbenzylstannic chloride* (KIPPING), 2368.

$C_{13}H_{13}O_2N$ Acetyl-2-methoxy-3-naphthylamine (CLEMO and SPENCE), 2818.

$C_{13}H_{13}O_2I$ 2-Phenyl-6-methyl-4-pyrone methiodide (GIBSON and SIMONSEN), 2310.

$C_{13}H_{13}O_3N_3$ Methyl 1-ketohydrindene-3-acetate semicarbazone (JACKSON and KENNER), 578.

$C_{13}H_{13}O_4N$ *iso*Nitroso-derivative of ethyl 1-ketohydrindene-3-acetate (JACKSON and KENNER), 578.

$C_{13}H_{14}ON_2$ 2-Aminomethoxydiphenylamines (MCCOMBIE, SCARBOROUGH, and WATERS), 357.

$C_{13}H_{14}O_2N_2$ Nitro-3-methyltetrahydrocarbazoles (PLANT and *Rosser*), 2457.

$C_{13}H_{14}O_3N_2$ 1-Acetyl-2-pyrrolidone-5-carboxyanilide (GRAY), 1266.

$C_{13}H_{14}NBr$ 7-Bromo-2:3:4:5-tetrahydroheptindole (PERKIN and PLANT), 2587.

$C_{13}H_{15}ON$ 8-Acetyltetrahydropentindole (PLANT and RIPPON), 1911.
Hexahydroacridone (PERKIN and PLANT), 2590.

$C_{13}H_{15}O_2N_3$ αα'-Dicyano-α-methyl*cyclo*pentane-1:1-diacet-*N*-methyl-
(BARDHAN), 2596.

1-*p*-Nitroanilino-1-cyano*cyclo*hexane (BETTS and PLANT), 2074.

$C_{13}H_{15}O_4Cl$ Ethyl phenylchloromalonate (FLÜRSCHEIM and HOLMES), 1613

$C_{13}H_{16}ON_2$ *Hexahydroacridoneoxime* (PERKIN and PLANT), 2590.

$C_{13}H_{16}O_4N_2$ 1-*p*-Nitroanilino*cyclo*hexane-1-carboxylic acid (BETTS and
2074.

$C_{13}H_{17}O_3N_3$ 1-*p*-Nitroanilino*cyclo*hexane-1-carboxyamide (BETTS and
2074.

$C_{13}H_{17}O_6N$ Diethyl hydrogen 3-amino-1-methyl*dicyclo*pentane-2:4:5-tricarb
(GOSS and INGOLD), 1277.

$C_{13}H_{18}O_2N_2$ 1-*p*-Aminoanilino*cyclo*hexane-1-carboxylic acid (BETTS and
2074.

αγ-Diacetylamino-β-phenylpropane (JACKSON and KENNER), 1659.

$C_{13}H_{19}O_2N$ Ethyl α-ethyl-Δ¹-*cyclo*hexenylcyanoacetate (McRAE and MA
486.

$C_{13}H_{20}O_4N_4$ 3:3'-Dimethoxydiphenylglutaric dihydrazide (JACKSON and KE
1661.

$C_{13}H_{20}O_5N_2$ *Dimethyl γ-xylonolactone phenylhydrazide* (HAWORTH and Pc
617.

2-Methylglucosephenylhydrazone (HICKINBOTTOM), 3146.

$C_{13}H_{21}O_4N$ Ethyl α-cyano-α-*iso*propylglutarate (HARIHARAN, MENON, and
SEN), 434.

$C_{13}H_{22}O_5N_4$ Di(ethyl acetoacetate)carbohydrazone (MUNRO and WILSON), 1

$C_{13}H_{25}OBr$ Methyl 11-bromodecoate (BHATTACHARYA, SALETORE, and SIMO
2680.

$C_{13}H_{26}ON_4$ Dipinacolincarbohydrazone (MUNRO and WILSON), 1259.

13 IV

$C_{13}H_4O_6N_2Br_2$ 2:7-Dibromo-4:6-dinitroxanthone (LE FÈVRE), 3251.

$C_{13}H_7O_5ClS$ Chloro-1:4-dihydroxythioxanthone dioxide (PRICE and S
3158.

$C_{13}H_8O_4NF$ Fluoronitrophenyl benzoates (HODGSON and NIXON), 1880.

$C_{13}H_8O_7N_5Cl$ Chlorodinitrohydroxybenzaldehyde *p*-nitrophenylhydrazones
SON and JENKINSON), 2274.

$C_{13}H_8O_7N_5Br$ Bromodinitrohydroxybenzaldehyde *p*-nitrophenylhyd
(HODGSON and JENKINSON), 2277.

$C_{13}H_8O_7N_5I$ *Iododinitrohydroxybenzaldehyde p-nitrophenylhydrazones* (H
and JENKINSON), 2279.

$C_{13}H_9ON_2Br_3$ 3:4':5'-Tribromo-4-methoxyazobenzene (BURNS, McCOMB
SCARBOROUGH), 2934.

$C_{13}H_9OClTe$ Chloromethylphenoxtellurine, and its salts (DREW), 510.

$C_{13}H_9O_3N_3Br$ Dibromonitrohydroxybenzaldehyde phenylhydrazones (H
and JENKINSON), 2278.

$C_{13}H_9O_3N_3Br_2$ Dibromohydroxybenzaldehyde *p*-nitrophenylhydrazones (H
and JENKINSON), 2275.

$C_{13}H_9O_5N_4Cl$ Chlorodinitrohydroxybenzaldehyde phenylhydrazones (HODG
JENKINSON), 2274.

Chloronitrohydroxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and J
SON), 2273.

$C_{13}H_9O_5N_4Br$ Bromodinitrohydroxybenzaldehyde phenylhydrazones (H
and JENKINSON), 2277.

Bromonitrohydroxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and J
SON), 2277.

$C_{13}H_9O_5N_4I$ Iododinitrohydroxybenzaldehyde phenylhydrazones (HODGSON and JENKINSON), 2279.

Iodonitrohydroxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and JENKINSON), 2279.

$C_{13}H_9O_6ClS$ Chloro-2:5-dihydroxydiphenylsulphone-2′-carboxylic acid (PRICE and SMILES), 3157.

$C_{13}H_{10}ON_2Cl_2$ 3:5-Dichloro-4-methoxyazobenzene (BURNS, MCCOMBIE, and SCARBOROUGH), 2934.

$C_{13}H_{10}ON_2Br_2$ 3:4′-Dibromo-4-methoxyazobenzene (BURNS, MCCOMBIE, and SCARBOROUGH), 2934.

$C_{13}H_{10}O_2N_2Br$ *m*-Nitrobenzylidene-*p*-bromoaniline (NISBET), 3123.

$C_{13}H_{10}O_2N_3Cl$ Chlorobenzaldehyde nitrophenylhydrazones (HODGSON and HANDLEY), 1885.

$C_{13}H_{10}O_3N_3Cl$ Chloronitrohydroxybenzaldehyde phenylhydrazones (HODGSON and JENKINSON), 2273.

$C_{13}H_{10}O_3N_3Br$ Bromonitrohydroxybenzaldehyde phenylhydrazones (HODGSON and JENKINSON), 2277.

$C_{13}H_{10}O_3N_3I$ Iodonitrohydroxybenzaldehyde phenylhydrazones (HODGSON and JENKINSON), 2279.

$C_{13}H_{10}O_7N_2S$ Nitro-*p*-tolyl *p*-nitrobenzenesulphonates (BELL), 2777.

$C_{13}H_{10}O_8N_4S$ *p*-Nitrobenzenesulphon-3:5-dinitro-*p*-tolylamide (BELL), 2777.

$C_{13}H_{11}ON_2Br$ 3-Bromo-4-methoxyazobenzene (BURNS, MCCOMBIE, and SCARBOROUGH), 2934.

$C_{13}H_{11}O_5NS$ *p*-Tolyl *p*-nitrobenzenesulphonate (BELL), 2777.

$C_{13}H_{12}O_4N_2S$ *p*-Nitrobenzenesulphon-*p*-tolylamide (BELL), 2777.

$C_{13}H_{14}ONP$ Phenylmethylphosphinanilide (GIBSON and JOHNSON), 96.

$C_{13}H_{14}O_2N_3Br$ α-Bromo-αα′-dicyano-α′-methyl*cyclo*pentane-1:1-diacetmethylimide (BARDHAN), 2599.

$C_{13}H_{16}ON_2S$ Acetyl derivative of 1-*n*-propylamino-3-methylbenzthiazole (HUNTER and STYLES), 3026.

$C_{13}H_{16}O_2N_2S$ Ethyl benziminazolyl-2-α-thiol-*n*-butyrate (STEPHEN and WILSON), 1419.

$C_{13}H_{19}O_6N_2As$ *m*-Nitrobenzopropylamidopropylarsinic acid (GOUGH and KING), 2442.

13 V

$C_{13}H_{14}O_7N_2SAs_2$ 3:3′-Diamino-4:4′-dihydroxyarsenobenzene-*NN*′-dimethylenesulphurous acid, and its sodium salt (NEWBERY and PHILLIPS), 125.

C_{14} Group.

$C_{14}H_{10}O$ 1-Phenanthrol (SHOESMITH and GUTHRIE), 2333.

$C_{14}H_{10}O_5$ *O*-Benzoylphloroglucinaldehyde, preparation and constitution of (ROBERTSON, ROBINSON, and STRUTHERS), 1455.

$C_{14}H_{12}O_2$ Benzoin, resolution of (HOPPER and WILSON), 2483.

$C_{14}H_{12}N_2$ 3-*o*-Aminophenylindole, and its salts (KERMACK and SLATER), 40.

$C_{14}H_{12}Cl_2$ 5:5′-Dichloro-3:3′-ditolyl (MCALISTER and KENNER), 1915.

$C_{14}H_{14}O$ Dibenzyl ether as a cryoscopic solvent (BENNETT and WILLIS), 2305.

Phenylbenzylcarbinol, resolution of, and its salts (GERRARD and KENYON), 2564.

$C_{14}H_{14}S_2$ 3:3′-Dimethylthioldiphenyl (BARBER and SMILES), 1147.

s-Diphenylthiolethane (BELL and BENNETT), 3190.

$C_{14}H_{14}O_2$ 4-Acetonyl-2:3-dimethyl-1:4-benzopyran (HILL), 257.

C H O Ethyl 1-keto-2-methyl-1:2:3:4-tetrahydronaphthalene-2-carboxylate

$C_{14}H_{16}O_4$ Ethyl *p*-carboxycinnamate (Titley), 2581.

$C_{14}H_{18}O_4$ Ethyl β-*o*-carboxyphenylpropionate (Titley), 2576.
Ethyl *m*-phenylenediacetates (Titley), 2579.
Ethyl β-veratrylcrotonate (Koepfli and Perkin), 2995.

$C_{14}H_{18}O_5$ Methyl β-*p*-methoxyphenylglutarate (Jackson and Kenner), 1660.

$C_{14}H_{18}O_7$ Methyl 5-methylethyl*dicyclo*pentan-3-one-1:2:4-tricarboxylate (Goss and Ingold), 1273.

$C_{14}H_{19}N$ Octahydroheptaquinoline (Perkin and Plant), 2588.

$C_{14}H_{22}O$ Aromadendrone (Briggs and Short), 2528.

$C_{14}H_{22}O_2$ 5-Acetyl-1-methyl-3:4-dipropenyl*cyclo*pentan-1-ol (Evans and Farmer) 1647.

$C_{14}H_{22}O_8$ Ethyl ethanetetracarboxylate, sodium salt, action of dibromotetracarboxylic esters on (Lennon and Perkin), 1513.

$C_{14}H_{22}O_9$ 3:4:6-Triacetyl β-ethylglucoside (Hickinbottom), 3145.

$C_{14}H_{24}O_4$ Diethyl α-methyl*cyclo*pentane-1:1-diacetate (Bardhan), 2599.

14 III

$C_{14}H_7ClBr_2$ 1-Chloro-9:10-dibromoanthracene (Cook), 2808.

$C_{14}H_8O_4Cl_2$ 5:5′-Dichlorodiphenyl-3:3′-dicarboxylic acid, and its salts (McAlister and Kenner), 1916.

$C_{14}H_8O_6N_2$ Dinitrobenzils (Chattaway and Coulson), 1086.

$C_{14}H_8O_9N_4$ *3:3′:4′:5-Tetranitro-4-methylbenzophenone* (Blakey and Scarborough), 2494.

$C_{14}H_9O_3N_3$ Nitro-3-phenylphthalazones (Rowe and Levin), 2553; (Rowe, Himmat, and Levin), 2561.

$C_{14}H_9O_4N$ Nitrobenzils (Chattaway and Coulson), 1084.

$C_{14}H_9O_4N_3$ 1:4-Diketo-3-(3′-*nitrophenyl*)-tetrahydrophthalazine (Rowe, Himmat and Levin), 2563.
1:4-Diketo-3-(4′-nitrophenyl)tetrahydrophthalazine (Rowe and Levin), 2554.

$C_{14}H_9O_7N_3$ 3:4′:5-Trinitro-4-methylbenzophenone (Blakey and Scarborough) 2493.

$C_{14}H_{10}O_2N_2$ 3-*o*-Nitrophenylindole (Kermack and Slater), 39.

$C_{14}H_{10}O_4S$ 2-Methoxythioxanthone dioxide (Price and Smiles), 3159.

$C_{14}H_{10}O_4Se_2$ 4:4′-Dicarboxydiphenyl diselenide (Gaythwaite, Kenyon, and Phillips), 2286.

$C_{14}H_{10}O_5N_2$ Dinitro-4-methylbenzophenones (Blakey and Scarborough), 2493.

$C_{14}H_{10}O_5S$ Methyl-1:4-dihydroxythioxanthone dioxide (Price and Smiles) 3158.

$C_{14}H_{10}O_6Se$ Disalicylyl selenide (Morgan and Burstall), 3270.

$C_{14}H_{10}N_4As_2$ Arsenobenziminazoles (Phillips), 3137.

$C_{14}H_{11}ON_3$ Amino-3-phenylphthalazones (Rowe and Levin), 2553; (Rowe, Himmat, and Levin), 2560.

$C_{14}H_{11}OBr$ 3-Bromo-4-methylbenzophenone (Blakey and Scarborough), 2492.

$C_{14}H_{11}O_2N$ 3′-Hydroxy-*N*-phenylphthalimidine (Rowe, Himmat, and Levin), 2561.

$C_{14}H_{11}O_2N_3$ 1-Benzoyloxy-6-methyl-1:2:3-benztriazole (Brady and Reynolds), 200.

$C_{14}H_{11}O_2Cl$ 4-Chlorodiphenylmethane-2′-carboxylic acid (Barnett and Wiltshire), 1823.

$C_{14}H_{11}O_3N$ 3-Nitro-4-methylbenzophenone (Blakey and Scarborough), 2492.

$C_{14}H_{11}O_4N_3$ *o*-Carboxybenzaldehyde-*p*-nitrophenylhydrazone (Rowe and Levin),

$_{14}H_{12}ON_2$ 3′-Amino-*N*-phenylphthalimidine (ROWE, HIMMAT, and LEVIN), 2560.

$_{14}H_{12}O_3N_2$ 5-Nitro-2-acetamidodiphenyl (BELL), 2774.
Nitroamino-4-methylbenzophenones (BLAKEY and SCARBOROUGH), 2493.

$_{14}H_{12}O_4S$ Methyl 2:5-dihydroxydiphenylsulphone-2′-carboxylate (PRICE and SMILES), 3157.

$_{14}H_{12}Cl_2S_2$ 4:4′-Dichloro-3:3′-dimethylthioldiphenyl (BARBER and SMILES), 1147.

$_{14}H_{12}I_2S_2$ Di-4-iodo-*m*-tolyl disulphide (BARBER and SMILES), 1144.

$_{14}H_{13}ON$ 3-Amino-4-methylbenzophenone, and its hydrobromide (BLAKEY and SCARBOROUGH), 2492.
Desylamines, hydrochlorides of (MCKENZIE and WALKER), 650.

$_{14}H_{13}OCl$ 5-Chloro-3-ethoxydiphenyl (HINKEL and HEY), 1204.

$_{14}H_{13}OBr$ 5-Bromo-3-ethoxydiphenyl (HINKEL and HEY), 1203.

$_{14}H_{13}O_2Cl$ 5-Chloro-4:4′-dihydroxy-3:3′-ditolyl (MORGAN and BURSTALL), 3268.

$_{14}H_{13}O_3N_3$ Methoxybenzaldehydenitrophenylhydrazones (HODGSON and HANDLEY), 1885.
3-Nitro-4′:5-diamino-4-methylbenzophenone (BLAKEY and SCARBOROUGH), 2494.

$_{14}H_{13}O_6Al$ Aluminosalicylic acid, and its salts (BURROWS and WARK), 225.

$_{14}H_{14}ON_2$ *N*-Acetyl-*p*-aminodiphenylamine (GIBSON and JOHNSON), 1286.

$_{14}H_{14}O_2S_2$ Diphenylthiolethane disulphoxides (BELL and BENNETT), 3190.

$_{14}H_{14}O_2Se$ Dihydroxydimethyldiphenyl selenides (MORGAN and BURSTALL), 3267.

$_{14}H_{14}O_3N_2$ Ethyl 2-methylquinoxaline-3-pyruvate (BENNETT and WILLIS), 1973.

$_{14}H_{14}O_4N_2$ Dinitrotolidines, isomerism of (LE FÈVRE and TURNER), 963.

$_{14}H_{14}N_2S$ Benzaldehyde-*p*-methylthiolphenylhydrazone (HODGSON and HANDLEY), 1886.

$_{14}H_{14}ClSb$ Di-*p*-tolylchlorostibine (GODDARD and YARSLEY), 720.

$_{14}H_{14}Cl_2Si$ Dibenzylsilicon dichloride, action of sodium on (STEELE and KIPPING), 1431.

$_{14}H_{14}Cl_3Sb$ Di-*p*-tolylstibine trichloride (GODDARD and YARSLEY), 721.

$_{14}H_{14}BrSb$ Di-*p*-tolylbromostibine (GODDARD and YARSLEY), 721.

$_{14}H_{14}ISb$ Di-*p*-tolyliodostibine (GODDARD and YARSLEY), 721.

$_{14}H_{15}ON$ Ketohexahydroheptaquinoline (PERKIN and PLANT), 2588.

$_{14}H_{15}O_2N$ *cyclo*Pentane-1-acetic-1-carboxylic acid (BARDHAN), 2600.

$_{14}H_{15}O_2Sb$ Di-*p*-tolylstibinic acid (GODDARD and YARSLEY), 721.

$_{14}H_{15}O_4N$ Ethyl phenylcyanomalonate (FLÜRSCHEIM and HOLMES), 2236.

$_{14}H_{16}O_3N_2$ Nitromethyl-ψ-indoxylspiro*cyclo*hexanes (BETTS and PLANT), 2072.

$_{14}H_{16}O_6S$ 2-Phenyl-6-methyl-4-pyrone methylmethosulphate (GIBSON and SIMONSEN), 2810.

$_{14}H_{17}ON$ Acetylhexahydroquinidenes (PERKIN and PLANT), 644.
Methyl-ψ-indoxylspiro*cyclo*hexanes (BETTS and PLANT), 2072.

$_{14}H_{17}O_3N$ 1-Carboxy*cyclo*pentane-1-acetanilic acid (VOGEL), 2022.
*cyclo*Pentane-1-acetic-1-carboxylic anilic acid (BARDHAN), 2600.

$_{14}H_{17}O_3N_3$ Ethyl 1-ketohydrindene-3-acetate semicarbazone (JACKSON and KENNER), 578.

$_{14}H_{19}ON$ αβ-Dimethylpentenoic-*p*-toluidides (ABBOTT, KON, and SATCHELL), 2519.

$_{14}H_{19}O_2N$ 1-Anilino-4-methyl*cyclo*hexane-1-carboxylic acid (BETTS and PLANT), 2073.
1-Toluidino*cyclo*hexane-1-carboxylic acids (BETTS and PLANT), 2071.

$_{14}H_{19}O_2Tl$ Thallium diethyl benzoylacetone (MENZIES, SIDGWICK, CUTCLIFFE,

$C_{14}H_{19}O_4N_3$ ααβ-Trimethyl-lævulic acid *p*-nitrophenylhydrazone (BARDHAN), 2616.

$C_{14}H_{22}O_5N_2$ *2:3:4-Trimethyl-lyxonic acid phenylhydrazide* (HIRST and SMITH), 3153.

Trimethyl-γ-xylonolactone phenylhydrazide (HAWORTH and PORTER), 617.

$C_{14}H_{22}O_6Mo$ Molybdyl bisdipropionylmethane (MORGAN and CASTELL), 3254.

Molybdyl bis-3-ethylacetylacetone (MORGAN and CASTELL), 3255.

$C_{14}H_{23}ON$ Aromadendrone oxime (BRIGGS and SHORT), 2528.

$C_{14}H_{23}ON_3$ *Δ¹-Pulegenylacetone semicarbazone* (JUPP, KON, and LOCKTON), 1643.

$C_{14}H_{23}O_4Br$ Ethyl α-bromo-α′-methyl*cyclo*pentane-1:1-diacetate (BARDHAN), 2599.

$C_{14}H_{24}O_6N_4$ Di(ethyl acetoacetate) dicarbohydrazone (MUNRO and WILSON), 1260.

$C_{14}H_{28}O_2N_6$ Dipinacolinhydrazidicarbohydrazone (MUNRO and WILSON), 1259.

14 IV

$C_{14}H_8ONCl$ *2′-Cyanodiphenyl-2-carboxylyl chloride* (BELL), 3248.

$C_{14}H_8O_7N_3Cl$ *4′-Chloro-3:3′:5-trinitro-4-methylbenzophenone* (BLAKEY and SCARBOROUGH), 2495.

$C_{14}H_9O_5NS$ 3-Keto-2-*p*-nitrophenyl-2:3-dihydrothionaphthen 1:1-dioxide (PRICE and SMILES), 2862.

$C_{14}H_9O_5N_2Cl$ Chlorodinitro-4-methylbenzophenones (BLAKEY and SCARBOROUGH), 2495.

$C_{14}H_9O_5N_2Br$ 3-Bromo-3′:5′-dinitro-4-methylbenzophenone (BLAKEY and SCARBOROUGH), 2494.

$C_{14}H_{10}OClBr$ 4′-Chloro-3-bromo-4-methylbenzophenone (BLAKEY and SCARBOROUGH), *2495.*

$C_{14}H_{10}O_2N_2I_2$ *3:5-Di-iodo-4-acetoxyazobenzene* (HUNTER and BARNES), 2067.

$C_{14}H_{10}O_3NCl$ Chloronitro-4-methylbenzophenones (BLAKEY and SCARBOROUGH), 2495.

$C_{14}H_{10}O_3NBr$ Bromonitro-4-methylbenzophenones (BLAKEY and SCARBOROUGH), 2494.

$C_{14}H_{10}O_4N_2Cl_2$ Dichlorodinitro-3:3′-dimethyldiphenyl (LE FÈVRE and TURNER), 968.

$C_{14}H_{10}O_4N_2Br_2$ Dibromodinitro-3:3′-dimethyldiphenyls (LE FÈVRE and TURNER), 967.

$C_{14}H_{11}ONCl$ Dichloroacetamidodiphenyls (HINKEL and HEY), 2790.

$C_{14}H_{11}ONBr_2$ 4:5-Dibromo-3-acetamidodiphenyl (HINKEL and HEY), 1840.

$C_{14}H_{11}O_2N_2Br$ 3-Bromo-4-acetoxyazobenzene (HUNTER and BARNES), 2064.

$C_{14}H_{11}O_2N_2I$ *3-Iodo-4-acetoxyazobenzene* (HUNTER and BARNES), 2064.

$C_{14}H_{11}O_2NS$ *m*-Tolyl *p*-nitrothiolbenzoate (BARBER and SMILES), 1147.

$C_{14}H_{11}O_6NS$ *o*-Carboxyphenyl-*p*-nitrobenzylsulphone (PRICE and SMILES), 2861.

p-Nitrobenzyl *o*-carboxybenzenesulphinate (PRICE and SMILES), 2861.

$C_{14}H_{12}ONCl$ 4′-Chloro-3-amino-4-methylbenzophenone (BLAKEY and SCARBOROUGH), 2495.

$C_{14}H_{12}ONBr$ *5-Bromo-3-acetylaminodiphenyl* (HINKEL and HEY), 1839.

Bromoamino-4-methylbenzophenones (BLAKEY and SCARBOROUGH), 2494.

$C_{14}H_{12}ON_3Cl$ 3-Chloro-4-acetamidoazobenzene (BURNS, MCCOMBIE, and SCARBOROUGH), 2928.

$C_{14}H_{12}O_2NCl$ Benzoyl derivative of 3-chloro-2-aminoanisole (HODGSON and KERSHAW), 192.

$C_{14}H_{12}O_4N_2S_4$ 4:4′-Dinitro-5:5′-dimethylthioldiphenyl disulphide (HODGSON and HANDLEY), 163.

$C_{14}H_{12}O_4N_2Se_2$ *Di*-2-nitro-*p*-tolyl diselenide (CHALLENGER and PETERS), 1369.

$C_{14}H_{12}O_4Cl_2S_2$ 4:4′-Dimethyldiphenyl-2:2′-disulphonyl chloride (BARBER and SMILES), 1147.

$C_{14}H_{12}O_6N_2S$ Dinitro-5:5-dimethoxydiphenyl sulphides (HODGSON and HANDLEY), 626.

$C_{14}H_{12}O_8N_2S$ Dinitro-5:5-dimethoxydiphenylsulphones (HODGSON and HANDLEY), 627.

$C_{14}H_{13}ONSe$ 4-Acetamidodiphenyl selenide (GAYTHWAITE, KENYON, and PHILLIPS), 2290.

$C_{14}H_{13}ON_2Cl$ Benzaldehyde-3-chloroanisyl-2-hydrazone (HODGSON and KERSHAW), 193.

*6-Chloro-5-benzeneazo-o-4-*xylenol (HINKEL, AYLING, and BEVAN), 2532.

$C_{14}H_{13}O_2NS$ 2-Benzenesulphonyldihydro*iso*indole (FENTON and INGOLD), 3295.

$C_{14}H_{13}O_2NSe$ 4-Acetamidodiphenyl selenoxide (GAYTHWAITE, KENYON, and PHILLIPS), 2291.

$C_{14}H_{13}O_2N_3S$ Methylthiobenzaldehydenitrophenylhydrazones (HODGSON and HANDLEY), 1885.

$C_{14}H_{13}O_3N_2Cl$ 6-Chloronitro-9-acetyltetrahydrocarbazole (PLANT and ROSSER), 2462.

$C_{14}H_{13}O_4NCl_4$ 6-Diacetamido-2:4-bisdichloromethyl-1:3-benzdioxin (CHATTAWAY and MORRIS), 3244.

$C_{14}H_{14}ONCl$ 6-Chloro-9-acetyltetrahydrocarbazole (PLANT and ROSSER), 2462.

$C_{14}H_{14}O_3N_2As_2$ 4-Amino-4′-acetamido-3:3′-dihydroxyarsenobenzene (BALABAN), 811.

$C_{14}H_{15}O_3NSe$ 4-Acetamidodiphenyl selenide dihydroxide (GAYTHWAITE, KENYON, and PHILLIPS), 2290.

$C_{14}H_{16}O_2N_2S_2$ Diamino-5:5-dimethoxydiphenyl disulphides (HODGSON and HANDLEY), 627.

$C_{14}H_{16}O_3NCl$ 6-Chloro-10:11-dihydroxy-9-acetylhexahydrocarbazole (PLANT and ROSSER), 2462.

$C_{14}H_{21}O_4N_2As$ γ-4-Benzoylpiperazinopropylarsinic acid (GOUGH and KING), 2445.

14 V

$C_{14}H_{10}O_2N_2ClBr$ 3-Chloro-5-bromo-4-acetoxyazobenzene (HUNTER and BARNES), 2065.

$C_{14}H_{10}O_2N_2ClI$ 3-Chloro-5-iodo-4-acetoxyazobenzene (HUNTER and BARNES), 2065.

$C_{14}H_{10}O_2N_2BrI$ 3-Bromo-5-iodo-4-acetoxyazobenzene (HUNTER and BARNES), 2066.

$C_{14}H_{12}ONClS$ 4-Chloro-2-thiobenzanisidine (HODGSON and HANDLEY), 163.

$C_{14}H_{13}ONCl_2Se$ 4-Acetamidodiphenyl selenide dichloride (GAYTHWAITE, KENYON, and PHILLIPS), 2292.

$C_{14}H_{13}ONBr_2Se$ 4-Acetamidodiphenyl selenide dibromide (GAYTHWAITE, KENYON, and PHILLIPS), 2292.

$C_{14}H_{13}ONI_2Se$ 4-Acetamidodiphenyl selenide di-iodide (GAYTHWAITE, KENYON, and PHILLIPS), 2293.

C_{15} Group.

$C_{15}H_{24}$ Aromadendrene, chemistry of (BRIGGS and SHORT), 2524.

Caryophyllene, reaction for (GIBSON), 750.

$C_{15}H_{26}$ Dihydroaromadendrene (BRIGGS and SHORT), 2527.

$C_{15}H_{28}$ Hexahydrocurcumene (RAO and SIMONSEN), 2504.

15 II

$C_{15}H_{10}O_4$ Purpuroxanthin 1-methyl ester (PERKIN and STOREY), 239.
$C_{15}H_{10}O_5$ Anthrapurpurin methyl ethers (PERKIN and STOREY), 235.
1:4-Diacetylpurpurin 2-methyl ether (PERKIN and STOREY), 238.
Genistein, synthesis of (BAKER and ROBINSON), 3115.
$C_{15}H_{10}O_6$ Irigenol, and its sulphate (BAKER), 1030.
$C_{15}H_{10}N_2$ 5:6-Benz-4-carboline (KERMACK and SLATER), 32.
$C_{15}H_{11}N$ 2:3-Indeno(1:2)-indole (TITLEY), 2576.
$C_{15}H_{11}Cl$ 2-Chloro-9-methylanthracene (BARNETT and WILTSHIRE), 1824.
$C_{15}H_{12}O_4$ ω-Hydroxy-4-benzoyloxyacetophenone (ROBERTSON and ROBINSO 1465.
α-Naphthylparaconic acid (SHOESMITH and GUTHRIE), 2332.
$C_{15}H_{14}N_2$ 3-*o*-*Aminophenyl-1-methylindole, and its salts* (KERMACK and SLATE 44.
$C_{15}H_{14}S_2$ Acetonediphenylene-2:2′-mercaptol (BARBER and SMILES), 1146.
$C_{15}H_{16}N_2$ 1-Cyano*cyclo*hexylphenylacetonitrile (McRAE and MANSKE), 490.
$C_{15}H_{19}N$ α-Phenyl-β-*n*-hexylacrylonitrile (McRAE and MANSKE), 490.
$C_{15}H_{20}O_4$ Ethyl γ-*o*-carbethoxyphenyl-*n*-butyrate (TITLEY), 2577.
Ethyl β-phenylglutarate (JACKSON and KENNER), 1658.
$C_{15}H_{20}O_6$ Methyl 3:3′-dimethoxydiphenylglutarate (JACKSON and KENNER), 16
$C_{15}H_{20}O_7$ Ethyl 5-methyl*dicyclo*penten-3-ol-1:2:4-tricarboxylate (GOSS and I GOLD), 1272.
$C_{15}H_{24}O$ Luparenol (CHAPMAN), 1304.
$C_{15}H_{24}O_3$ Ngaiol, isomeride of (McDOWALL), 1331.
$C_{15}H_{24}O_9$ 3:4:6-Triacetyl-2-methyl β-ethylglucoside (HICKINBOTTOM), 3145.
$C_{15}H_{25}Cl$ *l*-α-Curcumene hydrochloride (RAO and SIMONSEN), 2501.
$C_{15}H_{26}O_4$ *l*-Menthyl hydrogen glutarate (RULE, HAY, and PAUL), 1357.
$C_{15}H_{26}N_2$ Deoxylupanine, and its salts (CLEMO and LEITCH), 1818.
$C_{15}H_{28}O_3$ *l*-Menthyl propoxyacetate (RULE, HAY, and PAUL), 1355.
$C_{15}H_{30}O_3$ Substance, from hydrogenation of ngaiol (McDOWALL), 1327.
$C_{15}H_{32}O$ Substance, from reduction of tetrahydrongaiol (McDOWALL), 1329.

15 III

$C_{15}H_{10}ON_2$ 3-Keto-3:4-dihydro-5:6-benz-4-carboline (KERMACK and SLATER), 39
$C_{15}H_{10}O_4N_2$ 3-*o*-Nitrophenylindole-2-carboxylic acid, and its salts (KERMACK a SLATER), 38.
$C_{15}H_{10}N_2Br_2$ 3-Phenyl-2-ω-dibromomethylquinoxaline (BENNETT and WILLI 1974.
$C_{15}H_{11}O_2Cl$ Phenyl *p*-chlorobenzyl ketone (BENNETT and WILLIS), 1966.
$C_{15}H_{11}O_4N_3$ 4-Keto-1-methoxy-3-(3′-nitrophenyl)-3:4-dihydrophthalazine (ROW HIMMATT, and LEVIN), 2562.
4-Keto-1-methoxy-3-(4′-nitrophenyl)-3:4-dihydrophthalazine (ROWE and LEVI 2554.
$C_{15}H_{11}O_5Cl$ Pelargonidin chloride (ROBERTSON, ROBINSON, and SUGIURA), 1534.
$C_{15}H_{11}O_6Cl$ Cyanidin chloride (ROBERTSON and ROBINSON), 1528.
$C_{15}H_{12}O_2N_2$ 3-*o*-Nitrophenyl-1-methylindole (KERMACK and SLATER), 44.
$C_{15}H_{12}O_2Cl_2$ Benzoyldichloro-*o*-4-xylenols (HINKEL, AYLING, and BEVAN), 2537
$C_{15}H_{12}O_4N_2$ β-Phenylglutardiurethane (JACKSON and KENNER), 1658.
$C_{15}H_{12}O_5S$ Dimethoxythioxanthone dioxides (PRICE and SMILES), 3158.
$C_{15}H_{13}OCl$ *p*-Chlorophenyl β-phenylethyl ketone (BURTON and INGOLD), 920.
Phenyl β-*p*-chlorophenylethyl ketone (BURTON and INGOLD), 919

$C_{15}H_{13}OBr$ ω-Bromo-ω-benzylacetophenone (STEVENS, CREIGHTON, GORDON, and MACNICOL), 3197.

$C_{15}H_{13}O_2N$ 3′-Hydroxy-*N*-phenylphthalimidine methyl ether (ROWE, HIMMAT, and LEVIN), 2561.

$C_{15}H_{13}O_2N_3$ *iso*Nitroso-derivative of substance $C_{15}H_{14}ON_2$ (KRISHNAMURTI), 416.

$C_{15}H_{13}O_2Cl$ Benzoyl-3-chloro-*o*-4-xylenol (HINKEL, AYLING, and BEVAN), 2531.

$C_{15}H_{13}O_5N_3$ 3:5-Dinitro-4-acetomethylamidodiphenyl (BELL), 2776.

$C_{15}H_{14}ON_2$ Substance, *from aniline and benzoylacetonitrile* (KRISHNAMURTI), 416.

$C_{15}H_{14}O_6S$ 2:5-Dimethoxydiphenylsulphone-2′-carboxylic acid (PRICE and SMILES), 3157.

$C_{15}H_{15}N_3S$ Acetophenone δ-phenylthiosemicarbazone (STEPHEN and WILSON), 1422.

$C_{15}H_{16}O_3N_2$ Nitro-9-acetyl-3-methyltetrahydrocarbazole (PLANT and ROSSER), 2458.

$C_{15}H_{16}O_4S$ β-Phenoxyethyl *p*-tolueneesulphonate (PEACOCK and THA), 2305.

$C_{15}H_{17}ON$ 9-Acetyl-3-methyltetrahydrocarbazole (PLANT and ROSSER), 2458.

$C_{15}H_{17}O_2N$ 6-Acetyl-3-methyl-ψ-indoxyl*spirocyclo*pentane (PLANT and ROSSER), 2458.

$C_{15}H_{17}O_6N_3$ 5:5′-Dinitro-2′-piperidino-2-hydroxybenzophenone (LE FÈVRE), 3250.

$C_{15}H_{17}O_6P$ *αγ-Diphenoxyiso*propyl phosphate, and its sodium salt (BOYD and LADHAMS), 220.

$C_{15}H_{18}O_3N_2$ Ethyl 1-phenyl-3-methyl-5-pyrazone-4-β-propionate (CLEMO and WELCH), 2628.

*Nitrodimethyl-ψ-indoxylspirocyclo*hexanes (BETTS and PLANT), 2073.

$C_{15}H_{19}ON$ Acetylhexahydroheptindole (PERKIN and PLANT), 2587.

3:3:4:4-Tetramethyl*cyclo*pentane-1:2-dione anil (INGOLD and SHOPPEE), 396.

$C_{15}H_{19}O_3N$ 10:11-Dihydroxy-9-acetyl-3-methylhexahydrocarbazole (PLANT and ROSSER), 2458.

$C_{15}H_{20}O_2N_2$ Diacetyl-2:3:7-1:2:3:4-tetrahydroquinoxalines (GIBSON, NUTLAND and SIMONSEN), 111.

$C_{15}H_{21}ON$ ααβ-Trimethyl-Δβ-pentenoic *p*-toluidide (BARDHAN), 2616.

$C_{15}H_{21}O_2N$ 1-2′:4′-Dimethylanilino*cyclo*hexane-1-carboxylic acid (BETTS and PLANT), 2073.

Ethyl *trans*-decahydro-β-naphthylidenecyanoacetate (VOGEL), 2026.

$C_{15}H_{21}O_2Cl$ *d*-β-Octyl chlorobenzoates (RULE, HAY, NUMBERS, and PATERSON) 183.

$C_{15}H_{21}O_2Br$ *d*-β-Octyl *o*-bromobenzoate (RULE, HAY, NUMBERS, and PATERSON) 183.

$C_{15}H_{21}O_2I$ *d*-β-Octyl *o*-iodobenzoate (RULE, HAY, NUMBERS, and PATERSON) 183.

$C_{15}H_{21}O_4N_3$ Hydroxy-2:2:3:3-tetramethyl*cyclo*pentanone *p*-nitrophenylhydrazon (SHOPPEE), 1666.

$C_{15}H_{21}O_6N$ Ethyl 3-amino-1-methyl*dicyclo*pentane-2:4:5-tricarboxylate (GOSS an INGOLD), 1277.

$C_{15}H_{22}O_2N_2$ Oxylupanine (CLEMO and LEITCH), 1819.

$C_{15}H_{22}N_2S$ 1-*n*-Heptylamino-3-methylbenzthiazole (HUNTER and STYLES), 3027.

$C_{15}H_{23}ON$ *l*-Oximino-α-curcumene, and its hydrochloride (RAO and SIMONSEN 2501.

$C_{15}H_{23}O_2N$ Ethyl α-*n*-butyl-Δ¹-*cyclo*hexenylcyanoacetate (MCRAE and MANSKE 436.

Ethyl *r-trans*-dehydro-β-naphthylcyanoacetate (VOGEL),

$C_{15}H_{24}ON_2$ Lupanine, and its salts (CLEMO and LEITCH), 1

*iso*Lupanine (CLEMO and LEITCH), 1819.

$C_{15}H_{24}O_3N_2$ Caryophyllene nitrosite, rotation dispersion and circular dichroism o: (MITCHELL), 3258.

$C_{15}H_{24}N_2S$ *s-o*-Tolyl-*n*-heptylthiocarbamide (HUNTER and STYLES), 3026.

$C_{15}H_{25}ON_3$ Aromadendrone semicarbazone (BRIGGS and SHORT), 2528.

a-Methyl-*a*-Δ^1-pulegenylacetone semicarbazone (JUPP, KON, and LOCKTON), 1643.

$C_{15}H_{30}Cl_2Te_2$ Pentamethylene-*as*-bis*cyclo*telluripentane 1:1′-dichloride (MORGAN and BURGESS), 325.

$C_{15}H_{30}Br_2Te_2$ Pentamethylene-*as*-bis*cyclo*telluripentane 1:1′-dibromide (MORGAN and BURGESS), 326.

$C_{15}H_{30}Br_6Te_2$ Pentamethylene-*as*-bis*cyclo*telluripentane 1:1′-bisperbromide (MORGAN and BURGESS), 327.

$C_{15}H_{30}I_2Te_2$ Pentamethylene-*as*-bis*cyclo*telluripentane 1:1′-di-iodide (MORGAN and BURGESS), 328.

15 IV

$C_{15}H_{12}O_4N_2Cl_2$ 4-Methoxy*iso*phthalaldehydic acid 2:4-dichlorophenylhydrazone (CHATTAWAY and CALVET), 2916.

$C_{15}H_{13}O_6N_2Cl$ *aγ*-Di-*p*-nitrophenoxy*iso*propyl chloride (BOYD and LADHAMS), 221.

$C_{15}H_{14}ONCl$ *p*-Chlorophenyl *β*-phenylethyl ketone (BURTON and INGOLD), 920.

Phenyl *β*-*p*-chlorophenylethyl ketoxime (BURTON and INGOLD), 919.

$C_{15}H_{15}ONS_2$ 2:4-Dimethylthiolbenzanilide (HODGSON and HANDLEY), 164.

$C_{15}H_{15}O_2NS$ 2-*p*-Toluenesulphonyldihydro*iso*indole (FENTON and INGOLD), 3295.

$C_{15}H_{15}O_2N_2Br_3$ 4-2′:4′:6′-Tribromobenzeneazo-5-hydroxy-2:2:3:3-tetramethyl*cyclo*pentenone (SHOPPEE), 2364.

$C_{15}H_{15}O_4N_2Cl$ Ethyl 6-chloronitrotetrahydrocarbazole-9-carboxylate (PLANT and ROSSER), 2463.

$C_{15}H_{16}O_2NCl$ Ethyl 6-chlorotetrahydrocarbazole-9-carboxylate (PLANT and ROSSER), 2463.

$C_{15}H_{17}O_4NS$ Ethyl *a*-naphthalenesulphonylalanines (COLLES and GIBSON), 108.

$C_{15}H_{17}O_5N_2Cl$ Ethyl 6-chloro-11-nitro-10-hydroxyhexahydrocarbazole-9-carboxylate (PLANT and ROSSER), 2464.

$C_{15}H_{18}O_4NCl$ Ethyl 6-chloro-10:11-dihydroxyhexahydrocarbazole-9-carboxylate (PLANT and ROSSER), 2464.

$C_{15}H_{21}N_2BrS$ 5-Bromo-1-*n*-heptylamino-3-methylbenzthiazole (HUNTER and STYLES), 3027.

$C_{15}H_{21}N_2Br_3S$ 5-Bromo-1-*n*-heptylamino-3-methylbenzthiazole hydrobromide (HUNTER and STYLES), 3027.

$C_{15}H_{22}N_2Br_6S$ *s-o*-Tolyl-*n*-heptylthiocarbamide hexabromide (HUNTER and STYLES), 3027.

$C_{15}H_{23}N_2BrS$ *s*-5-Bromo-*o*-tolyl-*n*-heptylthiocarbamide (HUNTER and STYLES), 3027.

$C_{15}H_{30}N_7Te_2Cr_2$ Pentamethylene-*as*-bis*cyclo*telluripentane 1:1′-dichromate (MORGAN and BURGESS), 326.

C_{16} Group.

$C_{16}H_{10}O_5$ 3-Acetylpurpuroxanthin (PERKIN and STOREY), 236.

$C_{16}H_{12}O_5$ Anthrapurpurin 1:7-dimethyl ether (PERKIN and STOREY), 237.

Purpurin 2:4-dimethyl ether (PERKIN and STOREY), 238.

$C_{16}H_{12}N_2$ 3-Methyl-5:6-benz-4-carboline, and its salts (KERMACK and SLATER), 42.

Methylbenzcarbolines (KERMACK and SLATER), 795.

$C_{16}H_{13}N$ 1:2-Indolo(2:3)-3:4-dihydronaphthalene (TITLEY), 2577.

$C_{16}H_{13}Cl$ 2-Chloro-9-ethylanthracene (BARNETT and WILTSHIRE), 1824.
$C_{16}H_{14}O_5$ 2-Benzoyloxy-4:6-dimethoxybenzaldehyde (ROBERTSON, ROBINSON, and STRUTHERS), 1457.
$C_{16}H_{14}O_6$ 6:6′-Dimethoxydiphenic acid, and its alkaloid salts (KENNER and TURNER), 2342.
$C_{16}H_{16}O$ γ-Phenyl-α-*p*-tolylallyl alcohol (BURTON and INGOLD), 916.
$C_{16}H_{16}O_2$ *l*-αβ-Diphenylethyl acetate (GERRARD and KENYON), 2565.
$C_{16}H_{16}O_5$ *O*-Benzylsyringic acid (BRADLEY and ROBINSON), 1555.
$C_{16}H_{16}N_2$ 1-Phenyl-4-aminomethyl-3:4-dihydro*iso*quinoline (JACKSON and KENNER), 1660.
$C_{16}H_{17}N$ Hexahydro-αβ-naphthacarbazoles (OAKESHOTT and PLANT), 1844.
$C_{16}H_{18}O_5$ Piperonylidene-ααβ-trimethyl-lævulic acid (BARDHAN), 2616.
$C_{16}H_{18}S_2$ *s*-Di-*p*-tolylthiolethane (BELL and BENNETT), 3190.
$C_{16}H_{20}O_3$ Benzoyloxy-2:2:3:3-tetramethyl*cyclo*pentanones (SHOPPEE), 1668.
$C_{16}H_{20}O_6$ Ethyl phenylmethanetricarboxylate (FLÜRSCHEIM and HOLMES), 1612.
$C_{16}H_{20}O_8$ Ethyl trimethoxybenzoylacetoxyacetate (BRADLEY and ROBINSON), 1531.
$C_{16}H_{22}O_4$ Ethyl phenylenedipropionates (TITLEY), 2578, 2583.
d-β-Octyl hydrogen terephthalate (RULE, HAY, NUMBERS, and PATERSON), 183.
$C_{16}H_{22}O_5$ Ethyl β-*p*-methoxyphenylglutarate (JACKSON and KENNER), 1660.
$C_{16}H_{24}O_2$ *d*-β-Octyl toluates (RULE, HAY, NUMBERS, and PATERSON), 183.
$C_{16}H_{26}O_2$ Luparol (CHAPMAN), 1305.
$C_{16}H_{28}O_4$ *l*-Menthyl hydrogen adipate (RULE, HAY, and PAUL), 1358.
$C_{16}H_{30}O_3$ *l*-Menthyl *n*-butoxyacetate (RULE, HAY, and PAUL), 1356.

16 III

$C_{16}H_{10}O_4N_4$ 2-(2:4-Dinitrostyryl)quinoxaline (BENNETT and WILLIS), 1967.
$C_{16}H_{11}O_2N_3$ Nitrostyrylquinoxalines (BENNETT and WILLIS), 1967.
$C_{16}H_{11}O_2Cl$ 2-Chloro-9-anthranyl acetate (BARNETT and WILTSHIRE), 1824.
$C_{16}H_{11}O_4N$ *r*- and *l*-Phthalimidophenylacetic acids (MCKENZIE and WALKER), 648.
$C_{16}H_{12}ON_2$ 3-Keto-1-methyl-3:4-dihydro-5:6-benz-4-carboline (KERMACK and SLATER), 44.
$C_{16}H_{12}O_4N_2$ 3-*o*-Nitrophenyl-1-methylindole-2-carboxylic acid, and its salts (KERMACK and PERKIN), 43.
$C_{16}H_{12}O_4Cl_2$ Methyl 5:5′-dichlorodiphenyl-3:3′-dicarboxylate (MCALISTER and KENNER), 1916.
$C_{16}H_{12}ClBr$ 2-Chloro-10-bromo-9-ethylanthracene (BARNETT and WILTSHIRE), 1824.
$C_{16}H_{13}O_2N_3$ Acetamido-3-phenylphthalazones (ROWE and LEVIN), 2555; (ROWE, HIMMAT, and LEVIN), 2560.
$C_{16}H_{13}O_2N_5$ Diketosuccinimide phenylosazone (CHATTAWAY and HUMPHREY), 1096.
$C_{16}H_{13}O_2Cl$ Phenyl β-methoxy-*p*-chlorostyryl ketone (BENNETT and WILLIS), 1966.
$C_{16}H_{13}O_4N$ α-Phenylallyl *p*-nitrobenzoate (BURTON and INGOLD), 914.
$C_{16}H_{13}O_5N$ Benzyl *p*-nitrobenzoyloxymethyl ketone (BRADLEY and SCHWARZENBACH), 2906.
$C_{16}H_{13}O_5N_3$ 1-Hydroxy-3-(3′-nitrophenyl)-1:3-dihydrophthalazine-4-acetic acid (ROWE, HIMMAT, and LEVIN), 2559.
$C_{16}H_{13}O_6Cl$ Peonidin chloride (MURAKAMI and ROBINSON), 1539.
$C_{16}H_{13}O_9N_3$ 2:4-Dinitrophenylopianic oxime (BRADY, BAKER, GOLDSTEIN, and HARRIS), 536.

$C_{16}H_{14}O_2N_2$ 3′-Acetamido-*N*-phenylphthalimidine (ROWE, HIMMAT, and LEVIN), 2561.

$C_{16}H_{14}O_6Cu$ Methyl cuprisalicylate (DOAK and PACKER), 2766.

$C_{16}H_{14}O_4S_2$ *2:2′-Dicarboxymethylthioldiphenyl* (BARBER and SMILES), *1146.*

$C_{16}H_{14}O_5N_2$ 5-Carboxy-2-methoxyphenylglyoxylic acid phenylhydrazone (CHATTAWAY and CALVET), 2917.

$C_{16}H_{14}O_7Cu_2$ Methyl basic hydroxycuprisalicylate (DOAK and PACKER), 2767.

$C_{16}H_{14}N_4As_2$ 2:2′-Dimethylarsenobenziminazoles (PHILLIPS), 3137.

$C_{16}H_{15}O_2N$ 3-Acetamido-4-methylbenzophenone (BLAKEY and SCARBOROUGH), 2492.

3′-Hydroxy-*N*-phenylphthalimidine ethyl ether (ROWE, HIMMAT, and LEVIN), 2561.

$C_{16}H_{15}O_2N_3$ *iso*Nitroso-derivative, and its silver salt, of substance $C_{16}H_{14}ON$ (KRISHNAMURTI), 416.

$C_{16}H_{15}O_4Cl$ *O*-Benzylsyringoyl chloride (BRADLEY and ROBINSON), 1555.

$C_{16}H_{16}ON_2$ Substance, from *p*-toluidine and benzoylacetonitrile (KRISHNAMURTI), 416.

$C_{16}H_{16}O_4N_2$ *p*-Dimethylaminobenzyl nitrobenzoate (CLEMO and SMITH), 2424.

$C_{16}H_{16}O_6S$ Methyl 2:5-dimethoxydiphenylsulphone-2′-carboxylate (PRICE an SMILES), 3157.

$C_{16}H_{17}ON$ Ethyl benzyl-*p*-toluoylacetate oxime (BURTON and INGOLD), 920.

Phenyl β-p-tolylethyl ketoxime (BURTON and INGOLD), 921.

$C_{16}H_{17}ON_3$ Phenyl β-phenylethyl ketone semicarbazone (SHOPPEE), 2571.

$C_{16}H_{17}O_2N$ *N*-Benzoyl-*d*-ψ-ephedrine, and its hydrochloride (SIRCAR), 53.

p-Dimethylaminobenzyl benzoate (CLEMO and SMITH), 2424.

$C_{16}H_{17}O_2N_3$ 1-Hydroxy-3-(3′-aminophenyl)tetrahydrophthalazine-4-acetic aci (ROWE, HIMMAT, and LEVIN), 2560.

$C_{16}H_{17}O_4N$ *O*-Benzylsyringamide (BRADLEY and ROBINSON), 1556.

$C_{16}H_{18}O_2Br_2$ *p*-Bromobenzyl derivative of 1-bromo-2:2:3:3-tetramethyl-[0,1,2 *dicyclo*pentan-4-ol-5-one (INGOLD and SHOPPEE), 388.

$C_{16}H_{18}O_2S_2$ Dibenzylthiolethane disulphoxides (BELL and BENNETT), 3191.

Di-*p*-tolylthiolethane disulphoxides (BELL and BENNETT), 3191.

$C_{16}H_{18}O_4N_2$ Ethyl nitro-3-methyltetrahydrocarbazole-9-carboxylate (PLANT a *ROSSER*), *2459.*

$C_{16}H_{18}O_8Cu$ Methyl cuprisalicylate dihydrate (DOAK and PACKER), 2766.

$C_{16}H_{18}O_8Ni$ Methyl nickelosalicylate dihydrate (DOAK and PACKER), 2768.

$C_{16}H_{19}O_2N$ Acetylmethyl-ψ-indoxyl*spirocyclo*hexanes (BETTS and PLANT), 2072.

Ethyl 3-methyltetrahydrocarbazole-9-carboxylate (PLANT and ROSSER), 2459.

$C_{16}H_{19}O_3Br$ *p*-Bromobenzyl derivative of 2:2:3:3-tetramethyl-[0,1,2]-*dicyclo*penta 4-ol-5-one (INGOLD and SHOPPEE), 390.

$C_{16}H_{19}O_5N$ *p-Nitrobenzoyloxy-2:2:3:3-tetramethylcyclopentanone* (SHOPPEE), *166*

$C_{16}H_{19}O_8N$ Ethyl *o*-nitrophenyl methanetricarboxylate (FLÜRSCHEIM and HOLME 1616.

$C_{16}H_{21}O_3N$ *1-Carboxycycloheptane-1-acetanilic acid* (VOGEL), *2025.*

Hydroxy-2:2:3:3-tetramethyl*cyclo*pentanone oxime (SHOPPEE), 1668.

*cyclo*Pentane-1-acetic-1-carboxylic *p*-toluidide (BARDHAN), 2600.

$C_{16}H_{21}O_4N$ Ethyl 10:11-dihydroxy-3-methylhexahydrocarbazole-9-carboxyla (PLANT and ROSSER), 2460.

$C_{16}H_{22}O_3S$ Bornyl benzenesulphonates, decomposition and hydrolysis of (PATTERSON and MCALPINE), 2464.

$C_{16}H_{24}O_5N_2$ *β-p-Methoxyphenylglutaric diurethane* (JACKSON and KENNER), 166

$C_{16}H_{26}ON_2$ Methyl-lupanines, and their *hydrochlorides* (CLEMO and LEITCH), 1816.

$C_{16}H_{27}O_2N$ Ethyl α-cyano-α-*n*-butyl-Δ^{β}-nonenoate (McRAE and MANSKE), 488.

$C_{16}H_{29}N_2I$ Deoxylupanine methiodide (CLEMO and LEITCH), 1819.

$C_{16}H_{34}O_2S$ Di-*n*-octylsulphone (FENTON and INGOLD), 3130.

16 IV

$C_{16}H_{12}O_4NCl$ *p*-Chlorocinnamyl alcohol *p*-nitrobenzoate (BURTON), 1655.
α-*p*-Chlorophenylallyl alcohol *p*-nitrobenzoate (*BURTON*), *1655*.

$C_{16}H_{12}O_4N_2S$ 1-Benzenesulphonamido-8-nitronaphthalene (MILLS and ELLIOTT), 1298.

$C_{16}H_{12}O_4N_2As_2$ 3:3′-Dihydroxy-6:6′-arseno-1:4-benz*iso*oxazine (NEWBERY, PHILLIPS, and STICKINGS), 3056.

$C_{16}H_{13}O_7N_3S$ 1-3′-Nitrobenzeneazo-β-naphthaquinone-1-sulphonic acid, *sodium* salt (ROWE, HIMMAT, and LEVIN), 2558.

$C_{16}H_{14}O_4N_4As_2$ 8:8′-Diamino-3:3-dihydroxy-6:6′-arseno-1:4-benz*iso*oxazine (NEWBERY, *PHILLIPS*, and *STICKINGS*), *3060*.

$C_{16}H_{14}O_6N_4S_2$ 3:3′-Diacetamido-4:4′-dinitrodiphenyl disulphide (HODGSON and HANDLEY), 164.

$C_{16}H_{15}O_2NS$ Benzoyl-2-methyl-1-methylenebenzthiazole (CLARK), 2315.

$C_{16}H_{15}O_3NHg$ Acetoxymercuriacetamidodiphenyl (BELL), 2777.

$C_{16}H_{16}O_2N_2S_2$ 2:2′-Diacetamidodiphenyl disulphide (CLARK), 2319.

$C_{16}H_{16}O_2N_2As_2$ 6:6′-Arseno-(2:3-dihydro-1:4-benz*iso*oxazine) (NEWBERY, PHILLIPS, and STICKINGS), 3064.

$C_{16}H_{16}O_4N_2As_2$ Diacetamidodihydroxyarsenobenzenes (BALABAN), 811.

$C_{16}H_{17}O_2NS$ 2-*p*-Toluenesulphonyl-1-methyldihydro*iso*indole (FENTON and IN*GOLD*), *3296*.

$C_{16}H_{17}O_4NS_2$ *m*-Carboxyphenylethylsulphine-*p*-toluenesulphonylimine, and its resolution (HOLLOWAY, KENYON, and PHILLIPS), 3004.

$C_{16}H_{18}O_2NI$ Camphoroiodophenylimides (SINGH, AHUJA, and LAL), 2414.

$C_{16}H_{18}O_4NBr$ *p*-Nitrobenzyl derivative of 1-bromo-2:2:3:3-tetramethyl-[0,1,2]-*dicyclo*pentan-4-ol-5-*one* (*INGOLD and SHOPPEE*), *383*.

$C_{16}H_{20}O_3NI$ Iodocamphoranilic acids (SINGH, AHUJA, and LAL), 2413.

$C_{16}H_{20}O_6N_2Ni$ Methyl diamminenickelosalicylate (DOAK and PACKER), 2769.

$C_{16}H_{23}O_5NS$ Menthyl *p*-nitrobenzenesulphonate (BELL), 2777.

$C_{16}H_{24}O_5NCl$ Tetramethyl glucose *p*-chloroanilide (BAKER), 1982.

$C_{16}H_{24}O_5NBr$ Tetramethyl glucose *p*-bromoanilide (BAKER), 1982.

$C_{16}H_{25}O_6N_2As$ *m*-Nitrobenzoyl-γ-*n*-hexylaminopropylarsinic acid (GOUGH and KING), 2442.

$C_{16}H_{27}ON_2I$ Lupanine methiodide (CLEMO and LEITCH), 1816.

16 V

$C_{16}H_{13}O_4NCl_4S$ 2:4-Bisdichloromethyl-1:3-benzdioxin-6-sulphonanilide (CHATTAWAY and MORRIS), 3246.

C_{17} Group.

$C_{17}H_{14}O_4$ 4-Hydroxy-3:8-dimethoxyphenanthrene-5-carboxylactone (GULLAND and VIRDEN), 928.

$C_{17}H_{12}O_5$ 3-Acetylpurpuroxanthin 1-methyl ether (PERKIN and STOREY), 239.

$C_{17}H_{12}O_6$ 1-Acetylpurpurin 2-methyl ether (PERKIN and STOREY), 238.
2-Ethylcarbonatoalizarin (PERKIN and STOREY), 240.

$C_{17}H_{14}S_2$ 2-Phenyl*peri*naphtha-1:3-dithiane (PRICE and SMILES), 2374.

$C_{17}H_{14}O_2$ ω-3-Hydrindonylacetophenone (JACKSON and KENNER), 579.

$C_{17}H_{14}N_2$ 1:3-Dimethyl-5:6-benz-4-carboline (KERMACK and SLATER), 45.
3:4-Dimethyl-5:6-benz-4-ψ-carboline (KERMACK and SLATER), 796.
3-Ethyl-5:6-benz-4-carboline (KERMACK and SLATER), 42.
$C_{17}H_{15}O_2$ Benzoyl derivative of 4-phenyl-2-pyrrolidone (JACKSON and KENNER), 1659.
$C_{17}H_{15}Cl$ 2-Chloro-9-*n*-propylanthracene (BARNETT and WILTSHIRE), 1824.
$C_{17}H_{16}O_3$ Phenyl β:3-dimethoxystyryl ketone (BENNETT and WILLIS), 1967.
$C_{17}H_{16}O_5$ 2′:4′:6′-Trimethoxyphenylphthalide (LUND), 1573.
$C_{17}H_{16}O_6$ 2′:4′:6′-Trimethoxybenzoyl-*o*-benzoic acid (LUND), 1574.
$C_{17}H_{18}O_4$ 4-Benzyloxy-3:5-dimethylacetophenone (BRADLEY and ROBINSON), 1564.
$C_{17}H_{18}O_6$ Methyl *O*-benzylsyringate (BRADLEY and ROBINSON), 1555.
$C_{17}H_{20}O_2$ Benzoylcamphor, physical properties of (LOWRY, MACCONKEY, and BURGESS), 1333.
$C_{17}H_{20}N_2$ 1-(8′-Tetrahydropentindyl)-1-cyano*cyclo*pentane, and its picrate (PLANT and RIPPON), 1912.
$C_{17}H_{22}O_6$ Ethyl *p*-carbethoxybenzylmalonate (TITLEY), 2581.
$C_{17}H_{24}O_6$ Ethyl 3:3′-dimethoxydiphenylglutarate (JACKSON and KENNER), 1661.
$C_{17}H_{26}O_{10}$ 2:3:4:6-Tetra-acetyl β-*iso*propylglucoside (HICKINBOTTOM), 3146.
$C_{17}H_{30}O_4$ *l*-Menthyl hydrogen pimelate (RULE, HAY, and PAUL), 1358.
$C_{17}H_{31}N$ *l*-Dimethyldihydro-α-curcumenylamine (RAO and SIMONSEN), 2504.
$C_{17}H_{32}O_3$ *l*-Menthyl *n*-amyloxyacetate (RULE, HAY, and PAUL), 1356.

17 III

$C_{17}H_8O_3S$ 3:4-Naphthathioxanthone-1:2-quinone (PRICE and SMILES), 3159.
$C_{17}H_{10}O_5S$ 1:2-Naphthaquinone 2′-carboxyphenyl sulphoxide (PRICE and SMILES), 3159.
$C_{17}H_{11}O_2N_3$ 2-[Glyoxalinyl-4(5)]-5-naphthacinchoninic acid (HUBBALL and PYMAN), 26.
$C_{17}H_{11}O_4N_3$ 2-(2:4-Dinitrostyryl)-quinoline (BENNETT and WILLIS), 1973.
$C_{17}H_{11}O_6N_5$ 2-(2:4:6-Trinitrostyryl)-3-methylquinoxaline (BENNETT and WILLIS), 1970.
$C_{17}H_{12}OCl_2$ Dichlorostyryl ketones (HEILBRON and HILL), 2867.
$C_{17}H_{12}O_3Br_2$ 5:5′-Dibromo-2:2′-dihydroxydistyryl ketone (MCGOOKIN and SINCLAIR), 1173.
$C_{17}H_{12}O_3S$ *o*-Carboxyphenyl 2-hydroxy-α-naphthyl sulphide (PRICE and SMILES), 2863.
$C_{17}H_{12}O_4N_4$ 2-(2:4-Dinitrostyryl)-3-methylquinoxaline (BENNETT and WILLIS), 1970.
$C_{17}H_{12}O_7S$ 2:4-Diacetoxythioxanthone dioxide (PRICE and SMILES), 3158.
$C_{17}H_{13}OCl$ Chlorodistyryl ketones (HEILBRON and HILL), 2866.
$C_{17}H_{13}O_2N$ 3:3-Dimethoxythebenidine (GULLAND and VIRDEN), 927.
$C_{17}H_{13}O_2N_3$ 2-*m*-Nitrostyryl-3-methylquinoxaline (BENNETT and WILLIS), 1969.
$C_{17}H_{14}O_3N_2$ Diketosuccinanil *p*-tolylhydrazone (CHATTAWAY and HUMPHREY), 1098.
$C_{17}H_{14}O_8S$ 2:5-Diacetoxydiphenylsulphone-2′-carboxylic acid (PRICE and SMILES), 3157.
$C_{17}H_{15}O_2Cl$ Chlorohydroxy-β-phenylethyl styryl ketones (HEILBRON and HILL), 2866.
Phenylchlorophenylallyl acetates (BURTON and INGOLD), 918.
$C_{17}H_{15}O_4N$ α-3-Methylcinnamyl *p*-nitrobenzoate (BURTON), 1656.
4-Methylcinnamyl *p*-nitrobenzoate (BURTON and INGOLD), 9
α-*m*-Tolylallyl *p*-nitrobenzoate (BURTON), 1656.
α-*p*-Tolylallyl *p*-nitrobenzoate (BURTON and INGOLD), 915.

$C_{17}H_{15}O_{5}N_{3}$ Methyl 1-hydroxy-3-(3'-nitrophenyl)-1:3-dihydrophthalazine-4-acetate (ROWE, HIMMAT, and LEVIN), 2559.

$C_{17}H_{15}O_{6}Cl$ *5:7:4'-Trihydroxy-3':5'*-dimethoxyflavylium chloride (BRADLEY and ROBINSON), 1566.

$C_{17}H_{15}O_{7}Cl$ •Malvidin chloride (BRADLEY and ROBINSON), 1562.

$C_{17}H_{16}OS_{2}$ 2-Benzoyl-2-phenyl-1:3-dithian (CHIVERS and SMILES), 701.

$C_{17}H_{16}O_{2}N_{2}$ ω-3-Hydrindonylacetophenone dioxime (JACKSON and KENNER), 579.

$C_{17}H_{16}O_{2}Br_{2}$ αγ-Diphenylallyl bromides (BURTON and INGOLD), 916.

$C_{17}H_{16}O_{3}N_{2}$ 3-Hydroxy-2':5'-dimethoxy-2-benzylquinoxaline (GULLAND and VIRDEN), 1482.

$C_{17}H_{16}O_{4}N_{2}$ ω-Diazo-4-benzyloxy-3:5-dimethoxyacetophenone (BRADLEY and ROBINSON), 1560.

$C_{17}H_{17}ON$ Propionylacetophenoneanil (LOVETT and ROBERTS), 1977.

$C_{17}H_{17}O_{3}N_{3}$ Propionylacetophenone *p*-nitrophenylhydrazone (LOVETT and ROBERTS), 1977.

$C_{17}H_{17}O_{5}N$ *iso*Nitroso-4-benzyloxy-3:5-dimethoxyacetophenone (BRADLEY and ROBINSON), 1565.

$C_{17}H_{17}O_{5}N_{3}$ *5-Nitro-2-ethoxy-p-tolylglyoxylic acid phenylhydrazone* (CHATTAWAY and CALVET), 1093.

$C_{17}H_{18}ON_{2}$ Substance, from *m*-4-xylidine and benzoylacetonitrile (KRISHNAMURTI), 416.

$C_{17}H_{19}ON$ ω-Dimethylamino-ω-benzylacetophenone, and its picrate (STEVENS, CREIGHTON, GORDON, and MACNICOL), 3196.

$C_{17}H_{20}O_{4}S_{4}$ Propane αγ-di-*p*-toluenethiolsulphonate (CHIVERS and SMILES), 700.

$C_{17}H_{20}O_{6}S_{2}$ Trimethylene glycol di-*p*-toluenesulphonate (GOUGH and KING), 2446.

$C_{17}H_{21}O_{2}N$ 7-Acetyl-8:10-dimethyl-ψ-indoxyl*spirocyclo*hexane (BETTS and PLANT), 2078.

$C_{17}H_{21}O_{6}Cl$ Ethyl chloro-*p*-carbethoxybenzylmalonate (TITLEY), 2581.

$C_{17}H_{21}O_{4}P$ *Ditolyloxyisopropyl phosphates* (BOYD and LADHAMS), 219.

$C_{17}H_{22}ON_{2}$ 1-(8'-Tetrahydropentindyl)*cyclo*pentane-1-carboxyamide (PLANT and RIPPON), 1912.

$C_{17}H_{22}OSn$ Phenylbenzyl-*n*-butylstannic hydroxide, and its salts (KIPPING), 2371.

$C_{17}H_{23}O_{3}N$ Atropine, spontaneous resolution of sulphate of (ANDERSON and HILL), 993.

β-*cyclo*Hexylglutaranilic acid (SIRCAR), 56.

$C_{17}H_{24}ON_{2}$ 3:3:4:4-Tetramethyl*cyclo*pentane-1:2-dione *p*-dimethylanil (INGOLD and SHOPPEE), 396.

$C_{17}H_{27}O_{5}N$ Tetramethyl glucose *p*-toluidide (BAKER), 1982.

$C_{17}H_{27}O_{6}N$ Tetramethyl glucose *p*-anisidide (BAKER), 1982.

$C_{17}H_{29}ON$ Acetyl derivative of *l*-dihydro-α-curcumenylamine (RAO and SIMONSEN), 2503.

$C_{17}H_{29}O_{4}N$ *l*-Dihydro-α-curcumenylamine (RAO and SIMONSEN), 2502.

17 IV

$C_{17}H_{12}O_{2}N_{2}Cl_{6}$ 6-*p*-Tolueneazo-2:4-bistrichloromethyl-1:3-benzdioxin (CHATTAWAY and CALVET), 1092.

$C_{17}H_{20}O_{4}N_{2}S$ *5:6-Benz-4-carboline methosulphate* (KERMACK and SLATER), 795.

$C_{17}H_{20}ONBr$ Phenacylbenzyldimethylammonium bromide (STEVENS, CREIGHTON,

$C_{17}H_{24}ON_2S$ Acetyl derivative of 1-*n*-heptylamino-3-methylbenzthiazol (HUNTER and STYLES), 3027.

$C_{17}H_{30}ON_2I$ Methyl-lupanine methiodides (CLEMO and LEITCH), 1817.

$C_{17}H_{30}O_5N_2S$ Lupanine methosulphate (CLEMO and LEITCH), 1816.

C_{18} Group.

$C_{18}H_{12}O_7$ Diacetylanthrapurpurins (PERKIN and STOREY), 235.

$C_{18}H_{12}N_2$ 3:4′-Diquinolyl, and its picrate (MILLS and ORDISH), 85.

$C_{18}H_{14}O_6$ 1-Acetylpurpurin 2:4-dimethyl ether (PERKIN and STOREY), 238.
Ethylcarbonatoalizarin methyl ethers (PERKIN and STOREY), 240.

$C_{18}H_{15}N$ 2-Styryl-3-methylquinoline (BENNETT and WILLIS), 1973.

$C_{18}H_{16}O_4$ 5-Aldehydo-3:4:8-trimethoxyphenanthrene (GULLAND and VIRDEN 926.
Truxinic acid, synthesis of (VOGEL), 1021.

$C_{18}H_{16}O_5$ Ethyl benzoylhenzoyloxyacetate (BRADLEY and ROBINSON), 1548.
5:7:4′-Trimethoxy*iso*flavone (BAKER and ROBINSON), 3117.

$C_{18}H_{16}O_8$ Irigenin (BAKER), 1022.

$C_{18}H_{16}N_2$ *NN*′-Diphenyl-*o*-phenylenediamine (GIBSON and JOHNSON), 1988.

$C_{18}H_{18}O_2$ Phenyltolylallyl acetates (BURTON and INGOLD), 916.

$C_{18}H_{18}O_4$ 3:4:5:8-Tetramethoxyphenanthrene, and its picrate (GULLAND and VIRDEN), 1486.

$C_{18}H_{18}O_6$ ω-Benzoyloxy-3:4:5-trimethoxyacetophenone (BRADLEY and ROBINSON 1550.
Methyl 6:6′-dimethoxydiphenate (KENNER and TURNER), 2341.

$C_{18}H_{22}O_5$ *d*-Carene-β-glycol hydrogen phthalate (PILLAY and SIMONSEN), 362.

$C_{18}H_{22}N_2$ 1-(9′-Hexahydrocarbazyl)-1-cyano*cyclo*pentane (PLANT and RIPPON) 1909.

$C_{18}H_{24}O_6$ Ethyl carbethoxybenzylmethylmalonate (TITLEY), 2582.

$C_{18}H_{26}O_2$ 2-Hydroxystyryl nonyl ketone (HEILBRON and IRVING), 2326.

$C_{18}H_{32}O_4$ *l*-Menthyl hydrogen suberate (RULE, HAY, and PAUL), 1358.

$C_{18}H_{34}O_3$ *l*-Menthyl *n*-hexyloxyacetate (RULE, HAY, and PAUL), 1356.

18 III

$C_{18}H_{13}O_4N$ 2-Nitrostyryl-3-methylchromones (NISBET), 3122.

$C_{18}H_{13}O_4N_3$ 2-(2:4-Dinitrostyryl)methylquinolines (BENNETT and WILLIS), 197

$C_{18}H_{14}O_2N_2$ 2-Methylenedioxystyryl-3-methylquinoxaline (BENNETT and WILLIS 1968.

$C_{18}H_{15}O_2N_3$ 2-*m*-Nitrostyryl-3:6-dimethylquinoxaline (BENNETT and WILLIS 1972.

$C_{18}H_{15}O_3N$ 3:4:8-Trimethoxy-5-cyanophenanthrene (GULLAND and VIRDEN), 927

$C_{18}H_{16}ON_2$ 2-Methoxystyryl-3-methylquinoxalines (BENNETT and WILLIS), 196

$C_{18}H_{16}O_3N_2$ Nitroacetyltetrahydro-α′β′-naphthacarbazole (OAKESHOTT and PLANT 1846.

$C_{18}H_{17}ON$ Acetyltetrahydronaphthacarbazoles (OAKESHOTT and PLANT), 1843.
8-Benzoyltetrahydropentindole (PLANT and RIPPON), 1911.

$C_{18}H_{17}O_3Cl$ Ethyl benzyl-*p*-chlorobenzoylacetate (BURTON and INGOLD), 920.
Ethyl *p*-chlorobenzylbenzoylacetate (BURTON and INGOLD), 919.

$C_{18}H_{17}O_3Cl$ 5-Hydroxy-4′-methoxy-6:8-dimethylflavylium chloride (ROBERTSO ROBINSON, and STRUTHERS), 1458.

[illegible] ND and VI

$C_{18}H_{17}O_5N_3$ Ethyl 1-hydroxy-3-(3′-nitrophenyl)-1:3-dihydrophthalazine-4-acetate (ROWE, HIMMAT, and LEVIN), 2559.

$C_{18}H_{17}O_6Cl$ 5:7-Dihydroxy-3:3′:5′-trimethoxyflavylium chloride (ROBERTSON, ROBINSON, and SUGIURA), 1536.

$C_{18}H_{17}O_7Cl$ 3:5:7-Trihydroxy-3′:4′:5′-trimethoxyflavylium chloride (BRADLEY and ROBINSON), 1551.

$C_{18}H_{18}O_2N_2$ 3-Hydroxy-2-(6′-*methoxy-3′-ethylbenzyl*)*quinoxaline* (GULLAND and VIRDEN), 931.

$C_{18}H_{18}O_4N_2$ Methyl 3:4:8-trimethoxyphenanthrene-5-carboxylate hydrazide (GULLAND and VIRDEN), 926.

2′-Nitro-6:7-dimethoxy-1-benzyl-3:4-dihydro*iso*quinoline, and its hydrochloride (GULLAND and HAWORTH), 586.

$C_{18}H_{19}ON$ Acetylhexahydro-*αβ*-naphthacarbazoles (OAKESHOTT and PLANT), 1844.

$C_{18}H_{19}O_2N$ Hydroxyphenylthymylacetonitriles (BELL and HENRY), 2225.

$C_{18}H_{19}O_3N$ Catechylthymylacetonitrile (BELL and HENRY), 2226.

$C_{18}H_{19}O_4N_3$ 1-Hydroxy-3-(3′-acetamidophenyl)tetrahydrophthalazine-4-acetic acid (ROWE, HIMMAT, and LEVIN), 2560.

$C_{18}H_{20}O_5N_2$ 2′-Nitrophenylaceto-β-3:4-dimethoxyphenylethylamide (GULLAND and HAWORTH), 585.

$C_{18}H_{20}O_8N_4$ Dinitro-*NN′*-dicarbethoxybenzidines (LE FÈVRE and TURNER), 252.

$C_{18}H_{21}O_2N$ 1-(9′-Tetrahydrocarbazyl)*cyclo*pentane-1-carboxylic acid (PLANT and RIPPON), 1910.

$C_{18}H_{21}O_6N_3$ 2-Nitro-*NN′*-dicarbethoxybenzidine (LE FÈVRE and TURNER), 252.

$C_{18}H_{22}O_4N_2$ 4-*p*-Carbethoxybenzeneazo-5-hydroxy-2:2:3:3-tetramethyl-Δ^4-*cyclo*-pentenone (SHOPPEE), 2364.

$C_{18}H_{24}ON_2$ 1-(9′-Hexahydrocarbazyl)*cyclo*pentane-1-carboxyamide (PLANT and RIPPON), 1910.

$C_{18}H_{25}OCl$ Chlorostyryl nonyl ketones (HEILBRON and IRVING), 2326.

$C_{18}H_{34}NI$ *l*-Dihydro-α-curcumenyltrimethylammonium iodide (RAO and SIMONSEN), 2508.

18 IV

$C_{18}H_9O_3Br_7Se$ Tri-3:5-dibromotri-4-hydroxytriphenylselenonium bromide (MORGAN and BURSTALL), 3266.

$C_{18}H_{22}ONBr$ Phenacyl-β-phenylethyldimethylammonium bromide (STEVENS, CREIGHTON, GORDON, and MACNICOL), 3195.

$C_{18}H_{12}O_3Br_4Se$ Tri-3-bromotri-4-hydroxytriphenylselenonium bromide (MORGAN and BURSTALL), 3265.

$C_{18}H_{12}N_2Cl_2As_2$ Dichlorotetrahydro*iso*benzarsazinephenarsazines (GIBSON and JOHNSON), 2211.

$C_{18}H_{12}N_2Br_2As_2$ Dibromotetrahydrobenzarsazinephenarsazines (GIBSON and JOHNSON), 2213.

$C_{18}H_{12}N_2I_2As_2$ Di-iodotetrahydrobenzarsazinephenarsazine (GIBSON and JOHNSON), 2213.

$C_{18}H_{14}O_4N_2As_2$ Benzarsazinicphenarsazinic acids, and their sodium salts (GIBSON and JOHNSON), 2212.

$C_{18}H_{14}O_6N_2S$ *N*-Benzenesulphonyl-8-nitro-1-naphthylglycine, and its brucine salts (MILLS and ELLIOTT), 1299.

$C_{18}H_{15}O_3ClSe$ Trihydroxytriphenylselenonium chlorides (MORGAN and BURSTALL), 3266.

$C_{18}H_{15}O_6NSe$ Tri-4-hydroxytriphenylselenonium nitrate (MORGAN and BURSTALL), 3265.

$C_{18}H_{15}O_6ClSe$ Tri-2:4-dihydroxytriphenylselenonium chloride (MORGAN and BURSTALL), 3269.

$C_{18}H_{18}ON_4S$ Dibenzylidene derivative of 3-amino-2:4-diketo-5-methyltetrahydrothiazole 2-hydrazone (STEPHEN and WILSON), 1419.

$C_{18}H_{16}O_4N_2As_2$ 8:3′-Dihydroxy-8:8′-dimethyl-6:6′-arseno-1:4-benz*iso*oxazine (NEWBERY, PHILLIPS, and STICKINGS), 3061.

$C_{18}H_{18}O_4N_2S$ 1:4-Dimethyl-5:6-benz-4-carbolinium methyl sulphate (KERMACK and SLATER), 795.

3-Methyl-5:6-benz-4-carboline methosulphate (KERMACK and SLATER), 796.

$C_{18}H_{18}O_6N_2As_2$ 1:3-Phenylenediaminodi-*o*-phenylarsinic acid (GIBSON and JOHNSON), 2211.

$C_{18}H_{20}O_2N_2S_2$ 2:2′-Dipropionamidodiphenyl disulphide (CLARK), 2319.

$C_{18}H_{20}O_2N_2Se_2$ 2:2′-Diacetmethylamidodiphenyl diselenide (CLARK), 2317.

$C_{18}H_{20}O_4N_2S_2$ Diacetamido-5:5′-dimethoxydiphenyl disulphides (HODGSON and HANDLEY), 626.

$C_{18}H_{20}O_4N_2As_2$ 3:3′-Diacetamido-4:4′-dihydroxy-5:5′-dimethylarsenobenzene (NEWBERY, PHILLIPS, and STICKINGS), 3061.

$C_{18}H_{22}ONBr$ ω-Dimethylamino-ω-benzylacetophenone methobromide (STEVENS, CREIGHTON, GORDON, and MACNICOL), 3197.

$C_{18}H_{22}ONI$ Phenacylphenyldiethylammonium iodide (STEVENS, CREIGHTON, GORDON, and MACNICOL), 3195.

$C_{18}H_{22}O_4N_2S_4$ Dithianbis-*p*-toluenesulphonylimines (BELL and BENNETT), 92.

$C_{18}H_{44}O_{18}N_8Co_2$ Hexa-allylamineperoxodihydroxodicobalt trinitrate (BUCKNALL and WARDLAW), 2651.

18 V

$C_{18}H_{44}O_4N_6Cl_3Co_2$ Hexa-allylamineperoxodihydroxodicobalt trichloride (BUCKNALL and WARDLAW), 2649.

C_{19} Group.

$C_{19}H_{15}$ Triphenylmethyl, photodecomposition of (BOWDEN and JONES), 1149.

19 II

$C_{19}H_{14}O_7$ Diacetylanthrapurpurin methyl ethers (PERKIN and STOREY), 235.

$C_{19}H_{14}S_2$ Benzaldehydediphenylene-2:2′-mercaptal (BARBER and SMILES), 1146.

$C_{19}H_{16}O_7$ Trimethoxy*iso*flavonecarboxylic acid (BAKER and ROBINSON), 3117.

$C_{19}H_{18}O_2$ 4-Acetonyl-3-phenyl-2-methyl-1:4-benzopyran (HILL), 258.

4-Phenacyl-2:3-dimethyl-1:4-benzopyran (HILL), 258.

$C_{19}H_{18}O_6$ 2:3:5:6-Tetramethoxyphenanthrene-8-carboxylic acid (BARGER and SILBERSCHMIDT), 2922.

3:4:5:8-Tetramethoxyphenanthrene-9-carboxylic acid (GULLAND and VIRDEN) 1486.

Trimethylbrazilone (PERKIN, RÂY, and ROBINSON), 1510.

$C_{19}H_{20}O_3$ Ethyl benzyl-*p*-toluoylacetate (BURTON and INGOLD), 920.

Ethyl *p*-methylbenzylbenzoylacetate (BURTON and INGOLD), 920.

3:4:6-Trimethoxy-5-ethylphenanthrene (GULLAND and VIRDEN), 938.

$C_{19}H_{20}O_4$ Dihydrodeoxytrimethylbrazilone (PERKIN, RÂY, and ROBINSON), 1510.

$C_{19}H_{20}O_6$ ω-Acetoxy-4-benzyloxy-3:5-dimethoxyacetophenone (BRADLEY and ROBINSON), 1560.

Trimethyldihydrobrazilone (PERKIN, RÂY, and ROBINSON), 1512.

$C_{19}H_{22}O_4$ Tolylthymylacetic acid (BELL and HENRY), 2225.

$C_{19}H_{26}O_7$ Ethyl *p*-methoxyphenylpropane-ααγ-tricarboxylate (JACKSON and KENNER), 1660.

$C_{19}H_{34}O_4$ *l*-Menthyl hydrogen azelate (RULE, HAY, and PAUL), 1358.

$C_{19}H_{36}O_2$ Methyl elaidate, oxidation of (HILDITCH and LEA), 1576.

Methyl oleate, oxidation of (HILDITCH and LEA), 1576.

$C_{19}H_{36}O_3$ *l*-Menthyl *n*-heptyloxyacetate (RULE, HAY, and PAUL), 1856.
$C_{19}H_{40}O$ Octadecyl methyl ether (HEILBRON and OWENS), 1946.

19 III

$C_{19}H_{12}O_2N_2$ Diquinolyl-2-carboxylic acids (MILLS and ORDISH), 85.
$C_{19}H_{12}O_2Br_2$ 4:5-Dibromo-3-benzoyloxydiphenyl (HINKEL and HEY), 1203.
$C_{19}H_{13}O_2Br$ 5-Bromo-3-benzoyloxydiphenyl (HINKEL and HEY), 1203.
$C_{19}H_{15}O_4N$ 5-Keto-2-phenyl-4-(2′:5′-dimethoxybenzylidene)-4:5-dihydro-oxazole (GULLAND and VIRDEN), 1481.
$C_{19}H_{15}O_4N_3$ 6-Benzoylamino-3:4-dihydrocoumarin-4-cyanoacetamide (SESHADRI), 172.
$C_{19}H_{17}O_3N$ 5-Keto-2-phenyl-4-(6′-methoxy-3′-ethylbenzylidene)-4:5-dihydro-oxazole (GULLAND and VIRDEN), 980.
$C_{19}H_{18}ON_2$ 2-*p*-Methoxystyryl-3:6-dimethylquinoxaline (BENNETT and WILLIS), 1971.
$C_{19}H_{18}O_6N_2$ 2′-Nitro-3′:4′-dimethoxy-6:7-methylenedioxy-1-benzyl-3:4-dihydro*iso*quinoline, and its salts (GULLAND and HAWORTH), 1134.
2′-Nitro-6:3′:4′-trimethoxy-1-benzoyl-3:4-dihydro*iso*quinoline (GULLAND and HAWORTH), 2086.
$C_{19}H_{19}ON$ Benzoylhexahydroquinidenes (PERKIN and PLANT), 643.
$C_{19}H_{19}O_4N_3$ 5-Aldehydo-3:4:8-trimethoxyphenanthrene semicarbazone (GULLAND and VIRDEN), 926.
$C_{19}H_{19}O_5N$ 7:8:2′:5′-Tetramethoxy-3-phenylcarbostyril (GULLAND and VIRDEN), 1484.
$C_{19}H_{19}O_8N$ 2-Nitro-3:4:2′:5′-tetramethoxy-α-phenylcinnamic acids (GULLAND and VIRDEN), 1482.
$C_{19}H_{20}O_3N_6$ ω-3-Hydrindoxylacetophenone disemicarbazone (JACKSON and KENNER), 579.
$C_{19}H_{20}O_5N_2$ 2′-Nitro-6:3′:4′-trimethoxy-1-benzyl-3:4-dihydro*iso*quinoline, and its salts (GULLAND and HAWORTH), 2085.
$C_{19}H_{20}O_7N_2$ 2′-Nitro-3′:4′-dimethoxyphenylaceto-β-3:4-methylenedioxyphenylethylamide (GULLAND and HAWORTH), 1134.
$C_{19}H_{21}O_2N$ Anisylthymylacetonitrile (BELL and HENRY), 2225.
5:6-Dimethoxyaporphine, and its hydrochloride (GULLAND and HAWORTH), 590.
Tolylthymylacetonitrile (BELL and HENRY), 2225.
$C_{19}H_{21}O_3N_3$ 2-(4′:5′-Dimethoxy-2′-β-methylaminoethyl)phenyl-3-oximinoindole (GULLAND and HAWORTH), 588.
$C_{19}H_{21}O_4N$ Laurotetanine, constitution of (BARGER and SILBERSCHMIDT), 2919.
$C_{19}H_{21}O_6N$ 2-Amino-3:4:2′:5′-tetramethoxy-α-phenylcinnamic acids (GULLAND and VIRDEN), 1483.
$C_{19}H_{22}O_2N_2$ 2-(4′:5′-Dimethoxy-2′-β-methylaminoethyl)phenylindole, and its hydrochloride (GULLAND and HAWORTH), 587.
$C_{19}H_{22}O_6N_2$ 2′-Nitro-3′:4′-dimethoxyphenylaceto-β-3-methoxyphenylethylamide (GULLAND and HAWORTH), 2084.
$C_{19}H_{23}O_2N$ Diethylaminoethyl diphenylcarboxylates, and their hydrochlorides (BELL), 3248.
$C_{19}H_{23}O_2N$ Tolylthymylacetamide (BELL and HENRY), 2225.
$C_{19}H_{24}O_2N_2$ 2′-Amino-6:7-dimethoxy-1-benzyl-2-methyltetrahydro*iso*quinoline, and its hydrochloride (GULLAND and HAWORTH), 589.
2-(4′:5-Dimethoxy-2′-β-methylaminoethyl)phenyldihydroindole, and its hydrochloride (GULLAND and HAWORTH), 589.

19 IV

$C_{19}H_{12}O_2N_2I_2$ 3:5-Di-iodo-4-benzoyloxyazobenzene (HUNTER and BARNES), 2067.

$C_{19}H_{13}O_2N_2Br$ 3-Bromo-4-benzoyloxybenzene (HUNTER and BARNES), 2064.

$C_{19}H_{13}O_2N_2I$ 3-Iodo-4-benzoyloxyazobenzene (HUNTER and BARNES), 2065.

$C_{19}H_{14}O_8N_4S$ 3:5:4'-Trinitro-2-*p*-toluenesulphonamidodiphenyl (BELL), 2775.

$C_{19}H_{15}O_3N_2Cl$ 6-Chloronitro-9-benzoyltetrahydrocarbazole (PLANT and ROSSER 2463.

$C_{19}H_{15}O_6N_3S$ 3:5-Dinitro-*p*-toluenesulphonamidodiphenyls (BELL), 2774.

$C_{19}H_{16}ONCl$ 6-Chloro-9-benzoyltetrahydrocarbazole (PLANT and ROSSER), 2463.

$C_{19}H_{16}O_4N_2S$ Nitro-2-*p*-toluenesulphonamidodiphenyls (BELL), 2774.

$C_{19}H_{17}O_2NS$ 2-*p*-Toluenesulphonamidodiphenyl (BELL), 2774.

$C_{19}H_{17}O_4N_2Cl$ 6-Chloro-11-nitro-10-hydroxy-9-benzoylhexahydrocarbazole (PLAN and ROSSER), 2463.

$C_{19}H_{17}N_2IS$ 1':2-Dimethylthio-ψ-cyanine iodide (HAMER), 213.

$C_{19}H_{17}N_2ISe_2$ 2:2'-Dimethylselenocarbocyanine iodide (CLARK), 2318.

$C_{19}H_{18}ON_4S$ Dibenzylidene derivative of 3-amino-2:4-diketo-5-ethyltetrahydr thiazole 2-hydrazone (STEPHEN and WILSON), 1419.

$C_{19}H_{20}O_3NI$ Hydrohydrastinine phenacyloiodide (STEVENS, CREIGHTON, GORDO and MACNICOL), 3196.

$C_{19}H_{20}O_4N_2S$ 3-Ethyl-5:6-benz-4-carboline methosulphate (KERMACK and SLATER 797.

1:3:4-Trimethyl-5:6-benz-4-carbolinium methyl sulphate (KERMACK and SLATER 796.

$C_{19}H_{21}O_4N_2I$ 2'-Nitro-6:7-dimethoxy-1-benzyl-3:4-dihydro*iso*quinoline methiodi (GULLAND and HAWORTH), 586.

$C_{19}H_{26}O_5Br_2S$ Bromocamphorsulphonyl derivative of 1-bromo-2:2:3:3-tetramethy [0, 1, 2]-*dicyclo*pentan-4-ol-5-one (INGOLD and SHOPPEE), 387.

$C_{19}H_{29}ON_3Cl$ 2-Chlorostyryl nonyl ketone semicarbazone (HEILBRON and IRVING 2326.

19 V

$C_{19}H_{12}O_2N_2ClBr$ 3-Chloro-5-bromo-4-benzoyloxyazobenzene (HUNTER a BARNES), 2065.

$C_{19}H_{12}O_2N_2ClI$ 3-Chloro-5-iodo-4-benzoyloxyazobenzene (HUNTER and BARNES 2065.

$C_{19}H_{12}O_2N_2BrI$ 3-Bromo-5-iodo-4-benzoyloxyazobenzene (HUNTER and BARNES 2066.

$C_{19}H_{16}O_2NBrS$ 3-Bromo-4-*p*-toluenesulphonamidodiphenyl (BELL), 2778.

C_{20} Group.

$C_{20}H_{32}$ Dipinene, oxidation of (BRIGGS and SHORT), 3118.

20 II

$C_{20}H_{10}O_2$ 1:1'-Dinaphthylene 2:8':2':8-dioxide (CLEMO and SPENCE), 2815.

$C_{20}H_{10}O_3$ *o*-Dinaphthaquinone oxide (CLEMO and SPENCE), 2817.

*iso*Dinaphthaquinone oxide (CLEMO and SPENCE), 2817.

$C_{20}H_{12}O$ *1:1'-Dinaphthylene 2:2'-oxide* (CLEMO and SPENCE), *2815.*

*iso*Dinaphthylene oxide (CLEMO and SPENCE), 2816.

$C_{20}H_{12}O_4$ *Dihydroxydinaphthaquinone* (CLEMO and SPENCE), 2817.

$C_{20}H_{12}S$ 1:1'-Dinaphthylene 2:2'-sulphide (BARBER and SMILES), 1148.

$C_{20}H_{12}S_2$ *1:1'-Dinaphthylene 2:2'-disulphide* (BARBER and SMILES), *1148.*

$C_{20}H_{14}O_2$ β-Dinaphthol (CLEMO and SPENCE), 2815.

$C_{20}H_{14}O_4$ Phenolphthalein, constitution of (LUND), 1569.

$C_{20}H_{16}O_{9}$ 2:3-Diethylcarbonatoanthragallol (PERKIN and STOREY), 242.
2:7-Diethylcarbonatoanthrapurpurin (PERKIN and STOREY), 236.

$C_{20}H_{17}N$ 1:3-Diphenyldihydro*iso*indole, and its salts (BOYD and LADHAMS), 2093.

$C_{20}H_{18}O_{8}$ Methyl dibenzoyltartrate (FINDLAY and CAMPBELL), 1773.
r-βγ-Diphenylbutane-ααδδ-tetracarboxylic acid (VOGEL), 1019.

$C_{20}H_{20}O_{4}$ Dimethyl truxinate (VOGEL), 1021.
2:3:5:6-Tetramethoxy-8-vinylphenanthrene (BARGER and SILBERSCHMIDT), 2922.

$C_{20}H_{20}O_{5}$ 3:4:8-Trimethoxy-5-ethylphenanthrene-9-carboxylic acid (GULLAND and VIRDEN), 933.

$C_{20}H_{20}O_{8}$ Irigenin dimethyl ethers (BAKER), 1031.

$C_{20}H_{22}O_{6}$ Ethyl *O*-benzylsyringoylacetate, and its copper salt (BRADLEY and ROBINSON), 1557.

$C_{20}H_{24}N_{4}$ *pp'*-Tetramethyldiaminodiphenyl[glyoxalinyl-4(5)-]methane (HUBBALL and PYMAN), 26.

$C_{20}H_{28}O_{8}$ Ethyl β-3:4-dimethoxyphenylpropane-ααγ-tricarboxylate (JACKSON and KENNER), 1661.

$C_{20}H_{28}Sn$ Dibenzylethyl-*n*-butylstannane (KIPPING), 2372.

$C_{20}H_{30}O_{3}$ 3:4-Dimethoxystyryl nonyl ketone (HEILBRON and IRVING), 2324.

$C_{20}H_{36}O_{4}$ *l*-Menthyl hydrogen sebacate (RULE, HAY, and PAUL), 1358.

$C_{20}H_{38}O_{3}$ *l*-Menthyl *n*-octyloxyacetate (RULE, HAY, and PAUL), 1357.

20 III

$C_{20}H_{10}OBr_{2}$ Dibromo*iso*dinaphthylene oxide (CLEMO and SPENCE), 2816.

$C_{20}H_{12}O_{4}N_{4}$ 2:3-Di-*p*-nitrophenylquinoxaline (CHATTAWAY and COULSON), 1363.
2-*m*-Nitrophenyl-3-nitrophenylquinoxalines (CHATTAWAY and COULSON), 1087.

$C_{20}H_{12}I_{2}S_{2}$ Di-1-iodo-2-naphthyl disulphide (BARBER and SMILES), 1145.

$C_{20}H_{13}O_{2}N_{3}$ 2-*p*-Nitrophenyl-3-phenylquinoxaline (CHATTAWAY and COULSON), 1084.

$C_{20}H_{13}O_{4}Br$ Bromo-2-phenyl-6-piperonylidenemethyl-4-pyrone (GIBSON and SIMONSEN), 2312.

$C_{20}H_{14}O_{2}N_{2}$ 2:3-Di(β-furylvinyl)quinoxaline (BENNETT and WILLIS), 1969.

$C_{20}H_{14}O_{2}Se$ Di-2-hydroxydi-1-naphthyl selenide (MORGAN and BURSTALL), 3269.

$C_{20}H_{14}O_{4}S_{4}$ *1:1'-Dithiodinaphthalene-8:8'*-disulphinic acid (PRICE and SMILES), 2373.

$C_{20}H_{14}O_{5}N_{4}$ Dinitrobenzilphenylhydrazones (CHATTAWAY and COULSON), 1087, 1363.

$C_{20}H_{14}O_{6}S_{2}$ Bis-2'-carboxyphenylthiol-2:4-dihydroxybenzene (PRICE and SMILES), 2862.

$C_{20}H_{14}O_{6}S_{4}$ 1:1'-Dithiodinaphthalene-8:8'-disulphonic acid, and its sodium salt (PRICE and SMILES), 2372.

$C_{20}H_{15}ON$ 1-Hydroxy-1:3-diphenyl*iso*indole, and its hydrobromide (BOYD and LADHAMS), 2091.

$C_{20}H_{15}O_{3}N_{3}$ 4-Nitrobenzilphenylhydrazones (CHATTAWAY and COULSON), 1083.

$C_{20}H_{16}ON_{2}$ Nitroso-1:3-diphenyldihydro*iso*indole (BOYD and LADHAMS), 2093.

$C_{20}H_{16}O_{3}N_{2}$ Benzophenyl-3-nitrobenzylamide (REILLY, MOORE, and DRUMM), 564.

$C_{20}H_{17}OCl$ 3-Phenyl-5-chlorostyryl*cyclo*hexen-1-ones (HEILBRON and HILL),

$C_{20}H_{18}O_2S_2$ 1:3-Dibenzylthiolbenzene disulphoxides (BELL and BENNETT 3192.

$C_{20}H_{18}O_3N_2$ Nitro-9-benzoyl-3-methyltetrahydrocarbazole (PLANT and ROSSER 2459.

$C_{20}H_{18}O_4N_2$ 3-*o*-Carboxyphenylmethylcarbamyl-1:2-dimethyl-4-quinolone (HEI BRON, HOLT, and KITCHEN), 937.

$C_{20}H_{18}O_6Mo$ Molybdyl bisbenzoylacetone (MORGAN and CASTELL), 3255.

$C_{20}H_{18}O_{10}N_4$ 3:3'-Dinitrobenzidine (LE FÈVRE and TURNER), 252

$C_{20}H_{19}ON$ 9-Benzoyl-3-methyltetrahydrocarbazole (PLANT and ROSSER), 2459.

$C_{20}H_{19}O_2N$ Diacetyltetrahydro-α'β'-naphthacarbazole (OAKESHOTT and PLANT 1845.

$C_{20}H_{19}O_3N$ Thebenine, constitution of (GULLAND and VIRDEN), 921.

$C_{20}H_{19}O_4N$ 3:4-Dimethoxy-6-ethylbenzylidenehippuric acid azlactone (BARGE and SILBERSCHMIDT), 2925.

$C_{20}H_{19}O_4N_5$ Ethyl 2-methylquinoxaline-3-pyruvate *p*-nitrophenylhydrazo (BENNETT and WILLIS), 1978.

$C_{20}H_{19}O_7N_3$ 5:5'-Dinitro-2'-piperidino-2-acetoxybenzophenone (LE FÈVRE), 3251

$C_{20}H_{20}OSn$ Phenyl-*p*-tolylbenzylstannic hydroxide, and its salts (KIPPING), 237

$C_{20}H_{20}O_4N_2$ 11-Nitro-10-hydroxy-9-benzoyl-3-methylhexahydrocarbazole (PLAN and ROSSER), 2459.

$C_{20}H_{20}O_7N_2$ Substance, from *o*-nitrobenzyl chloride and ethyl acetoacetate (KE MACK and SLATER), 36.

$C_{20}H_{21}ON$ Benzoylhexahydroheptindole (PERKIN and PLANT), 2587.
9-Benzoyl-3-methylhexahydrocarbazole (PLANT and ROSSER), 2461.

$C_{20}H_{21}O_2N$ β-Naphthylimide of α-methyl*cyclo*pentane-1:1-diacetic acid (BARDHAN 2597.

$C_{20}H_{21}O_4N$ Bulbocapnine methyl ether (GULLAND and HAWORTH), 1136.

$C_{20}H_{21}O_7N$ *trans*-α(6'-Methoxy-3'-ethylphenyl)-2-nitro-3:4-dimethoxycinnam acid, and its ammonium salt (GULLAND and VIRDEN), 931.

$C_{20}H_{22}ON_2$ Acetyl-α-*NN'*-dimethyl-2-phenylnaphthylene-1:3-diamine (GIBSO KENTISH, and SIMONSEN), 2136.

$C_{20}H_{22}O_2N_2$ Diethylaminoethyl-2'-cyanodiphenyl-2-carboxylate, and its hydr chloride (BELL), 3249.
Ethyl 3-ketophenheptamethylene-2-carboxylate phenylhydrazone (TITLEY 2578.

$C_{20}H_{22}O_5N_2$ 2'-Nitro-6:3':4'-trimethoxy-1-benzylidene-2-methyltetrahydro*is* quinoline (GULLAND and HAWORTH), 2085.

$C_{20}H_{22}O_6N_2$ 2'-Nitro-6:7:3':4'-tetramethoxy-1-benzyl-3:4-dihydro*iso*quinoline, an its salts (GULLAND and HAWORTH), 1836.

$C_{20}H_{23}O_3N$ Morphothebaine dimethyl ethers, and their salts (GULLAND an HAWORTH), 2087.
β-Naphthylamic acid of α-methyl*cyclo*pentane-1:1-diacetic acid (BARDHAN 2597.
dl-3:4:6-Tetramethoxyaporphine, and its hydriodide (GULLAND and HAWORTH 2086.

$C_{20}H_{23}O_5N$ *trans*-α(6'-Methoxy-3'-ethylphenyl)-2-amino-3:4-dimethoxycinnam acid (GULLAND and VIRDEN), 932.

$C_{20}H_{24}O_3S$ Bornyl naphthalenesulphonates, decomposition and hydrolysis of (PA TERSON and MCALPINE), 2464.

$C_{20}H_{24}O_4N_2$ 2'-Amino-3':4'-dimethoxy-6:7-methylenedioxy-1-benzyl-2-methyltetr hydro*iso*quinoline, and its dihydrochloride (GULLAND and HAWORTH), 1135.

$C_{20}H_{24}O_7N_2$ 2' Nitro-3':4'-dimethoxyphenylaceto-β-3:4-dimethoxyphenylethy amide (GULLAND and HAWORTH), 1834.

$C_{20}H_{25}O_9N$ Tetra-acetylglucoseanilide (BAKER), 1

$C_{20}H_{26}O_3N_2$ 2′-Amino-6:3′:4′-trimethoxy-1-benzyl-2-methyltetrahydro*iso*quinoline, and its dihydrochloride (GULLAND and HAWORTH), 2086.

20 IV

$C_{20}H_{12}O_4Cl_2S_2$ 1:1′-Dinaphthyl-2:2′-disulphonic acid (BARBER and SMILES), 1148.
$C_{20}H_{17}O_6N_3S$ 3:5-Dinitro-4-*p*-toluenesulphonmethylamidodiphenyl (BELL), 2776.
$C_{20}H_{18}O_4N_2S$ 5-Nitro-2-*p*-toluenesulphonmethylamidodiphenyl (BELL), 2775.
$C_{20}H_{18}O_6N_2S$ Ethyl *N*-benzenesulphonyl-8-nitro-1-naphthylaminoacetate (MILLS and ELLIOTT), 1299.
$C_{20}H_{18}O_6N_4As_2$ 8:8′-Diacetamido-3:3′-dihydroxy-6:6′-arseno-1:4-benz*iso*oxazine (NEWBERY, PHILLIPS, and STICKINGS), 3060.
$C_{20}H_{19}O_2NS$ 2-*p*-Toluenesulphonmethylamidodiphenyl (BELL), 2774.
$C_{20}H_{19}N_2IS$ Methylethylthio-ψ-cyanine iodides (HAMER), 214.
$C_{20}H_{19}N_2IS_2$ 2.2′:8-Trimethylthiocarbocyanine iodide (HAMER), 3162.
$C_{20}H_{20}ON_4S$ 3-Phenylmethylmethyleneamino-2:4-diketo-5-methyltetrahydrothiazole 2-phenylmethylmethylenehydrazone (STEPHEN and WILSON), 1418.
$C_{20}H_{21}O_6N_2I$ 2′-Nitro-3′:4′-dimethoxy-6:7-methylenedioxy-1-benzyl-3:4-dihydro*iso*quinoline methiodide (GULLAND and HAWORTH), 1135.
$C_{20}H_{24}O_2NI$ 5:6-Dimethoxyaporphine methiodide (GULLAND and HAWORTH), 590.
$C_{20}H_{24}O_9NCl$ Tetra-acetylglucose-*p*-chloroanilide (BAKER), 1590.
$C_{20}H_{24}O_9NBr$ Tetra-acetylglucose *p*-bromoanilide (BAKER), 1590.
$C_{20}H_{26}O_8N_4As_2$ 3:3′-Di(β-hydroxyethylamino)-5:5′-diacetamido-4:4′-dihydroxyarsenobenzene (NEWBERY, PHILLIPS, and STICKINGS), 3064.

20 V

$C_{20}H_{13}O_3NClBr$ Chlorobromobenzamidophenyl benzoates (HUNTER and BARNES), 2060.
$C_{20}H_{13}O_3NClI$ 2-Chloro-6-iodo-4-benzamidophenyl benzoate (HUNTER and BARNES), 2066.
$C_{20}H_{13}O_3NBrI$ Bromoiodobenzamidophenyl benzoates (HUNTER and BARNES), 2062.

C_{21} Group.

$C_{21}H_{12}O_2$ Dinaphthaxanthone (CLEMO and SPENCE), 2819.
$C_{21}H_{12}O_3$ 9-*o*-Carboxyphenyl-9-hydroxyanthrone lactone (COOK), 63.
$C_{21}H_{12}O_6$ 2-Benzoylanthrapurpurin (PERKIN and STOREY), 237.
$C_{21}H_{14}O_2$ 9-*o*-Carboxyphenylanthracene (COOK), 64.
Semipinacolin, from benzylideneanthrone dibromide and silver oxide (COOK), 58
$C_{21}H_{14}O_3$ 9-*o*-Carboxyphenylanthrone (COOK), 64.
$C_{21}H_{14}O_4$ Lactonic acid of triphenylcarbinol-2:2′-dicarboxylic acid (COOK), 64.
$C_{21}H_{14}O_4$ 2-Benzoylbenzophenone-2′-carboxylic acid (COOK), 62.
$C_{21}H_{15}Cl$ 2-Chloro-9-benzylanthracene (BARNETT and WILTSHIRE), 1324.
Chloro-9-benzylanthracenes (COOK), 2806.
$C_{21}H_{16}O_2$ Substance, from reduction of semipinacolin, $C_{21}H_{14}O_2$ (COOK), 61.
$C_{21}H_{18}O_9$ Diethylcarbonatoanthragallol methyl ethers (PERKIN and STOREY), 242.
2:7-Diethylcarbonatoanthrapurpurin 1-methyl ether (PERKIN and STOREY), 236.
$C_{21}H_{22}O_8$ Ethyl 3:4:5-trimethoxybenzoylbenzoyloxyacetate (BRADLEY and ROBINSON), 1549.
$C_{21}H_{32}O$ 4-*iso*Propylstyryl nonyl ketone (HEILBRON and IRVING), 2325.
$C_{21}H_{44}O_3$ Batyl alcohol (HEILBRON and OWENS), 944.

21 III

C[illegible]H[illegible]O[illegible]S 2-Quinizarinophenylsulphone-2′-carboxylic acid (PRICE and SMILES),

$C_{21}H_{14}O_6S$ 2-Toluene-*p*-sulphonylalizarin (PERKIN and STOREY), 241.

$C_{21}H_{14}ClBr$ 2-Chloro-10-bromo-9-benzylanthracene (BARNETT and WILTSHIRE), 1624.

Chlorobromo-9-benzylanthracenes (COOK), 2806.

1-Chloro-10-bromo-9-benzylidene-9:10-dihydroanthracene (COOK), 2806.

$C_{21}H_{14}ClBr_3$ 2-Chloro-10-bromo-9-benzylanthracene dibromide (BARNETT and WILTSHIRE), 1825.

$C_{21}H_{15}OCl$ 4-Chloro-ω-hydroxy-9-benzylanthracene (COOK), 2809.

1-Chloro-10-hydroxy-9-benzylidene-9:10-dihydroanthracene (COOK), 2807.

$C_{21}H_{15}N_2Cl$ 2-*p*-Chlorobenzyl-3-phenylquinoxaline (BENNETT and WILLIS), 196.

$C_{21}H_{16}OCl_2$ 1:5-Dichloro-9-benzyl-9:10-dihydroanthranol (BARNETT and COOK), 572.

$C_{21}H_{17}OCl$ 1-Chloro-9-hydroxy-9-benzyl-9:10-dihydroanthracene (COOK), 2806.

$C_{21}H_{18}O_2N_2$ Homophthalanilide (DAVIES and POOLE), 1619.

$C_{21}H_{18}I_3Sb$ Tri-*m*-iodo-*p*-tolylstibine (GODDARD and YARSLEY), 723.

$C_{21}H_{19}O_2I$ 1:1′-Dimethyl*iso*cyanine iodide (HAMER), 213.

$C_{21}H_{20}O_4N_2$ 3-*o*-Carbomethoxyphenylmethylcarbamyl-1:2-dimethyl-4-quinolone (HEILBRON, HOLT, and KITCHEN), 987.

$C_{21}H_{21}O_{10}Cl$ 3-β-Glucosidylpelargonidin chloride (ROBERTSON and ROBINSON), 1469.

$C_{21}H_{21}ClSn$ Tri-*m*-tolylstannic chloride (KIPPING), 2369.

$C_{21}H_{22}ON_2$ Acetyl-*NN*′-trimethyl-2-phenylnaphthylene-1:3-diamine (GIBSON, KENTISH, and SIMONSEN), 2141.

$C_{21}H_{22}O_2N_2$ Strychnine, constitution of (FAWCETT, PERKIN, and ROBINSON), 3082.

$C_{21}H_{23}ON$ *Benzoyloctahydroheptaquinoline* (PERKIN and PLANT), 2583.

$C_{21}H_{23}O_8N$ *a-3:4-Dimethoxy-6-ethylphenyl-β-6-nitro-3:4-dimethoxyphenylacrylic acid* (BARGER and SILBERSCHMIDT), 2926.

$C_{21}H_{24}O_3N_2$ *Acetyl derivative of 2-(4′:5′-dimethoxy-2′-β-methylaminoethyl)*phenylindole (GULLAND and HAWORTH), 587.

$C_{21}H_{24}N_3Sb$ Tri-*m*-aminotri-*p*-tolylstibine (GODDARD and YARSLEY), 722.

$C_{21}H_{25}O_4N$ *dl*-Corytuberine dimethyl ether (GULLAND and HAWORTH), 1836.

$C_{21}H_{26}O_3N_2$ 2′-Acetylamino-6:7-*dimethoxy*-1-*benzyl*-2-*methyltetrahydroiso*quinoline (GULLAND and HAWORTH), 589.

$C_{21}H_{27}O_9N$ Tetra-acetylglucose-*N*-methylanilide (BAKER), 1590.

Tetra-acetylglucose-*p*-toluidide (BAKER), 1589.

$C_{21}H_{27}O_{10}N$ Tetra-acetylglucose-*p*-anisidide (BAKER), 1590.

$C_{21}H_{28}O_4N_2$ 2′-Amino-6:7:3′:4′-tetramethoxy-1-benzyl-2-methyltetrahydro*iso*quinoline, and its dihydrochloride (GULLAND and HAWORTH), 1836.

$C_{21}H_{28}O_4N_4$ Trimethylfructose phenylosazone (HAWORTH and LEARNER), 623

21 IV

$C_{21}H_{16}O_8N_2S$ Nitrobenzyl esters of carboxyphenyl-*p*-nitrobenzylsulphones (F and SMILES), 2861.

$C_{21}H_{18}O_3Br_4Se$ *Tribromotrihydroxytrimethyltriphenylselenonium bromides* (OAN and BURSTALL), 3267.

$C_{21}H_{18}O_7N_3Sb$ Tri-*m*-nitrotri-*p*-tolylstibine *oxide* (GODDARD and YARSLEY),

$C_{21}H_{18}O_{12}N_5Sb$ Tri-*m*-nitrotri-*p*-tolylstibine dinitrate (GODDARD and YARS 722.

$C_{21}H_{20}O_3N_2Cl_2$ 4-Chloro-3-*o*-carbomethoxyphenylmethylcarbamyl-2-methylquinoline methochloride (HEILBRON, HOLT, and KITCHEN), 989.

$C_{21}H_{21}O_6NSe$ Tri-4-hydroxytri-3-methyltriphenylselenonium nitrate (MORGAN and BURSTALL), 3267.

$C_{21}H_{21}N_2IS$ 1′:2-Diethylthio-ψ-cyanine iodide (HAMER), 213.

$C_{21}H_{21}N_2ISe_2$ 2:2′-Diethylselenocarbocyanine iodide (CLARK), 2318.

$C_{21}H_{22}ON_4S$ * 3-Phenylmethylmethyleneamino-2:4-diketo-5-ethyltetrahydrothiazole 2-phenylmethylmethylenehydrazone (STEPHEN and WILSON), 1418.

$C_{21}H_{24}O_4NI$ Bulbocapnine methyl ether methiodide (GULLAND and HAWORTH), 1137.

$C_{21}H_{25}O_6N_2I$ 2′-Nitro-6:7:3′:4′-tetramethoxy-1-benzyl-3:4-dihydro*iso*quinoline methiodide (GULLAND and HAWORTH), 1836.

21 V

$C_{21}H_{20}O_3N_2ClI$ 4-Chloro-3-*o*-carbomethoxyphenylmethylcarbamyl-2-methylquinoline methiodide (HEILBRON, HOLT, and KITCHEN), 939.

$C_{21}H_{21}O_3Cl_3SeHg$ Tri-4-methoxytriphenylselenonium mercurichloride (MORGAN and BURSTALL), 3265.

C_{22} Group.

$C_{22}H_{14}O_5$ 1-Benzoylalizarin 2-methyl ether (PERKIN and STOREY), 240.

$C_{22}H_{16}O$ 2-Benzylidene-3-phenyl-Δ³-benzopyran (DICKINSON, HEILBRON, and O'BRIEN), 2080.

$C_{22}H_{16}O_4$ Methyl 2-benzoylbenzophenone-2′-carboxylate (COOK), 62.

$C_{22}H_{16}O_5$ ω:4-Dibenzoyloxyacetophenone (ROBERTSON and ROBINSON), 1466.

$C_{22}H_{16}N_2$ 2-Styryl-3-phenylquinoxaline (BENNETT and WILLIS), 1972.

$C_{22}H_{16}Cl_2$ 1:5-Dichloro-9-benzyl-10-methylene-9:10-dihydroanthracene (BARNETT and COOK), 570.

$C_{22}H_{18}O_2$ 2-Hydroxy-α-phenylstyryl benzyl ketone (DICKINSON, HEILBRON, and O'BRIEN), 2080.

$C_{22}H_{18}O_5$ Resorcinolphenolphthalein 2′:4′-dimethyl ether (LUND), 1575.

$C_{22}H_{18}O_9$ *O*-Triacetylbrazilone (PERKIN, RÂY, and ROBINSON), 1513.

$C_{22}H_{22}O_8$ Ethyl dibenzoyltartrate (FINDLAY and CAMPBELL), 1774.

$C_{22}H_{22}O_9$ Acetylirigenin 7:3′-dimethyl ether (BAKER), 1031.

$C_{22}H_{24}O_7$ Ethyl *O*-benzoylsyringoylacetoacetate (BRADLEY and ROBINSON), 1556.

$C_{22}H_{24}Sn$ Triphenyl-*n*-butylstannane (KIPPING), 2370.

$C_{22}H_{28}O_3$ Menthyl methoxynaphthoates (BRETSCHER, RULE, and SPENCE), 1500.

$C_{22}H_{40}O_2$ Behenolic acid, synthesis of (BHATTACHARYA, SALETORE, and SIMONSEN), 2678.

22 III

$C_{22}H_{14}O_4N_4$ 2-(2:4-Dinitrostyryl)-3-phenylquinoxaline (BENNETT and WILLIS), 1972.

$C_{22}H_{15}O_2N_3$ 2-*p*-Nitrostyryl-3-phenylquinoxaline (BENNETT and WILLIS), 1972.

2-(β-Phenyl-*p*-nitrostyryl)quinoxaline (BENNETT and WILLIS), 1972.

$C_{22}H_{15}O_6Cl$ Benzoylpelargonidin chloride (ROBERTSON, ROBINSON, and SUGIURA), 1534.

$C_{22}H_{15}O_7Cl$ Benzoylcyanidin chloride (ROBERTSON and ROBINSON), 1528.

$C_{22}H_{16}O_{12}N_6$ Ethyl αβ-bis-2:4-dinitrophenyl-αβ-dicyanosuccinate (FAIRBOURNE and FAWSON), 1079.

$C_{22}H_{17}OCl$ Chloro-ω-methoxy-9-benzylanthracenes (COOK), 2808.

1-Chloro-10-methoxy-9-benzylidene-9:10-dihydroanthracene (COOK), 2808.

$C_{22}H_{17}O_2N_5$ Diketosuccinanil phenylosazone (CHATTAWAY and HUMPHREY), 1097.

$C_{22}H_{17}O_4N$ *r*- and *l*-Desylphthalamic acids (MCKENZIE and WALKER), 649.

$C_{22}H_{18}O_2N_6$ Diketosuccinophenylhydrazide phenylosazone (CHATTAWAY and HUMPHREY), 1097.

$C_{22}H_{18}O_4N_4$ 1-Hydroxy-3-(3′-nitrophenyl)-1:3-dihydrophthalazine-4-acetanilid (ROWE, HIMMAT, and LEVIN), 2559.

$C_{22}H_{19}O_3N_5$ Diketosuccinanilic acid phenylosazone (CHATTAWAY and HUMPHREY), 1097.

$C_{22}H_{20}O_8S_2$ Ditoluene-*p*-sulphonylgallacetophenone (PERKIN and STOREY), 243.

$C_{22}H_{21}N_2I$ Methylethyl-ψ-cyanine iodide (HAMER), 210.

Trimethyl-ψ-cyanine iodide (HAMER), 211.

$C_{22}H_{22}O_2N_2$ Diacetyl-β-*NN*′-dimethyl-2-phenylnaphthylene-1:3-diamine (GIBSON, KENTISH, and SIMONSEN), 2140.

$C_{22}H_{22}O_4N_2$ 3-*o*-Carbethoxyphenylmethylcarbamyl-1:2-dimethyl-4-quinolone (HEILBRON, HOLT, and KITCHEN), 937.

$C_{22}H_{22}N_2I_2$ 3:4′-Diquinolyl diethiodide (MILLS and ORDISH), 85.

$C_{22}H_{23}O_5N$ Oxydehydrocorydaline (KOEPFLI and PERKIN), 2999.

$C_{22}H_{23}N_2I$ 1:3:3:1′-Tetramethylindo-ψ-cyanine iodide (HAMER), 214.

$C_{22}H_{24}O_5N_2$ 1-αγ-Ditolyl*iso*propylpyridinium nitrates (BOYD and LADHAMS), 220.

$C_{22}H_{27}ON$ *l*-Benzoyloximino-α-curcumene (RAO and SIMONSEN), 2502.

$C_{22}H_{27}O_2N$ Dicarvacrylacetonitrile (BELL and HENRY), 2224.

Dithymylacetonitrile (BELL and HENRY), 2224.

Thymylcarvacrylacetonitrile (BELL and HENRY), 2224.

$C_{22}H_{27}O_4N$ Dimethyl-laurotetaninemethine, and its hydriodide (BARGER and SILBERSCHMIDT), 2921.

$C_{22}H_{29}O_2N$ Dithymylacetamide (BELL and HENRY), 2224.

$C_{22}H_{30}ON_2$ *d*- and *l*-β-2:3:7-Trimethyl-1:2:3:4-tetrahydroquinoxalino-1-methylenecamphor (GIBSON, NUTLAND, and SIMONSEN), 114.

$C_{22}H_{31}O_{16}N_3$ Substance, *from hydrolysis of substance* $C_{33}H_{40}O_{16}N$ (HENRY and SHARP), 1115.

$C_{22}H_{32}ON_2$ *l*-α-Curcumenenitrolbenzylamine (RAO and SIMONSEN), 2501.

22 IV

$C_{22}H_{13}O_2N_5Cl_4$ Diketosuccinanil 2:4-dichlorophenylosazone (CHATTAWAY and HUMPHREY), 1098.

$C_{22}H_{13}O_2N_5Br_4$ Diketosuccinanil 2:4-dibromophenylosazone (CHATTAWAY and HUMPHREY), 1098.

$C_{22}H_{14}O_2N_6Cl_4$ Diketosuccinophenylhydrazide 2:4-dichlorophenylhydrazone (CHATTAWAY and HUMPHREY), 1098.

$C_{22}H_{14}O_2N_6Br_4$ Diketosuccinophenylhydrazide 2:4-dibromophenylosazone (CHATTAWAY and HUMPHREY), 1098.

$C_{22}H_{16}O_6N_2S_2$ 1-Dibenzenesulphonamido-8-nitronaphthalene (MILLS and ELLIOTT), 1299.

$C_{22}H_{20}O_4N_2Br_2$ 6-Bromo-3-*p*-bromo-*o*-carbethoxyphenylmethylcarbamyl-1:2-dimethyl-4-quinolone (HEILBRON, HOLT, and KITCHEN), 941.

$C_{22}H_{22}O_3N_2Cl_2$ 4-Chloro-3-*o*-carbethoxyphenylmethylcarbamyl-2-methylquinoline methochloride (HEILBRON, HOLT, and KITCHEN), 938.

$C_{22}H_{22}O_7N_2Cl_2$ 4-Chloro-3-*o*-carbethoxyphenylmethylcarbamyl-2-methylquinoline methoperchlorate (HEILBRON, HOLT, and KITCHEN), 938.

$C_{22}H_{23}N_2IS_2$ 8-Methyl-2:2′-diethylthiocarbocyanine iodide (HAMER), 3162.

$C_{22}H_{24}O_3NCl$ *1-αγ-Di-p-tolylisopropylpyridinium chlorate* (BOYD and LADHAMS), 220.

$C_{22}H_{26}O_2N_2Br_2$ Diphenacyldimethylpiperazinium dibromide (STEVENS, CREIGHTON, GORDON, and MACNICOL), 3196.

$C_{22}H_{28}O_4NI$ *dl*-Corytuberine dimethyl ether methiodide (GULLAND and HAWORTH), 1837.

22 V

$_{22}H_{23}O_3N_2Cl_2Br_2$ 4-Chloro-6-bromo-3-*p*-bromo-*o*-carbethoxyphenylmethylcarbamyl-2-methylquinoline methochloride (HEILBRON, HOLT, and KITCHEN), 941.

$_{22}H_{23}O_3N_2ClI$ 4-Chloro-3-*o*-carbethoxyphenylmethylcarbamyl-2-methylquinoline methiodide (HEILBRON, HOLT, and KITCHEN), 938.

C_{23} Group.

$_{23}H_{14}O_6$ 2-Benzoyl-1-acetylalizarin (PERKIN and STOREY), 239.

$_{23}H_{16}O_5$ *o*-Benzoylphenylacetoxyphthalide (COOK), 62.

$_{23}H_{16}O_6$ Benzoylanthrapurpurin dimethyl ethers (PERKIN and STOREY), 237.

$_{23}H_{18}O_3$ *o*-Hydroxybenzylidenephenylacetylacetophenone (LOVETT and ROBERTS), 1977.

$_{23}H_{20}O_2$ 2-Methoxy-*α*-phenylstyryl benzyl ketone (DICKINSON, HEILBRON, and O'BRIEN), 2080.

$_{23}H_{20}O_6$ Phloroglucinolphenolphthalein 2′:4′:6-trimethyl ether (LUND), 1575.

$_{23}H_{26}Sn$ Diphenylbenzyl-*n*-butylstannane (KIPPING), 2371.

$_{23}H_{28}O_2$ Menthyl diphenyl-2-carboxylate (BRETSCHER, RULE, and SPENCE), 1502.

$_{23}H_{28}O_{12}$ *ω*-*O*-Tetra-acetyl-*β*-glucosidoxy-4-methoxyacetophenone (ROBERTSON and ROBINSON), 1467.

23 III

$_{23}H_{16}O_7N_4$ Trinitrobenzoyltetrahydro-*αβ*-naphthacarbazole (OAKESHOTT and PLANT), 1843.

$_{23}H_{17}O_2Cl$ Chloro-*ω*-acetoxy-9-benzylanthracenes (COOK), 2808.

1-Chloro-10-acetoxy-9-benzylidene-9:10-dihydroanthracene (COOK), 2807.

$_{23}H_{17}O_5Cl$ 7-Hydroxy-5-benzoyloxy-4′-methoxyflavylium chloride (ROBERTSON, ROBINSON, and STRUTHERS), 1458.

$_{23}H_{17}O_7Cl$ 5-*O*-Benzoylpeonidin chloride (MURAKAMI and ROBINSON), 1538.

$_{23}H_{18}O_2N_2$ 3-Phenyl-2-phenylacetoxymethylquinoxaline (BENNETT and WILLIS), 1974.

$_{23}H_{18}O_3N_2$ Nitrobenzoyltetrahydro-*α′β′*-naphthacarbazole (OAKESHOTT and PLANT), 1846.

$_{23}H_{19}ON$ Benzoyltetrahydronaphthacarbazoles (OAKESHOTT and PLANT), 1843.

$_{23}H_{19}OCl$ 4-Chloro-*ω*-ethoxy-9-benzylanthracene (COOK), 2810.

$_{23}H_{19}O_2N_5$ Diketosuccinobenzylimide phenylosazone (CHATTAWAY and HUMPHREY), 1096.

$_{23}H_{20}O_2N_6$ Diketosuccinophenylhydrazide *o*-tolylphenylosazone (CHATTAWAY and HUMPHREY), 1098.

Diketosuccinophenylmethylhydrazide phenylosazone (CHATTAWAY and HUMPHREY), 1098.

$_{23}H_{20}O_3Cl_2$ Ethyl 3-chlorophenyl-5-chlorostyryl*cyclo*hexen-1-one-2-carboxylates (HEILBRON and HILL), 2869.

$_{23}H_{21}ON$ Benzoylhexahydro-*αβ*-naphthacarbazoles (OAKESHOTT and PLANT), 1844.

$_{23}H_{21}O_2N_3$ 2-Hydroxy-*α*-phenylstyryl benzyl ketone semicarbazone (DICKINSON, HEILBRON, and O'BRIEN), 2080.

$_{23}H_{21}O_3N$ Dibenzoylnor-*d*-*ψ*-ephedrine (SMITH), 53.

$_{23}H_{21}O_3Cl$ Ethyl 3-phenyl-5-chlorostyryl*cyclo*hexen-1-one-2-carboxylates (HEILBRON and HILL), 2868.

$_{23}H_{22}O_2N_2$ *αγ*-Dibenzoylamino-*β*-phenylpropane (JACKSON and KENNER), 1659.

$_{23}H_{22}O_8S_2$ Ditoluene-*p*-sulphonylgallacetophenone methyl ether (PERKIN and STOREY), 248.

$_{23}H_{23}O_2N_3$ Benzoin-*δ*-(*α*-phenylethyl)semicarbazone (HOPPER and WILSON), 2486.

$C_{23}H_{23}O_4Cl$ Ethyl (γ-keto-α-phenyl-ε-2-chlorophenyl-Δδ-pentenyl)acetoa (HEILBRON and HILL), 2868.
$C_{23}H_{23}N_2I$ 1:1′-Diethyl*iso*cyanine iodide (HAMER), 213.
1:1′-Diethyl-ψ-cyanine iodide (HAMER), 212.
1:6:1′:6′-Tetramethyl-ψ-cyanine iodide (HAMER), 211.
$C_{23}H_{25}O_4N$ *Acetyltolylacetylthymylacetonitrile* (*BELL and HENRY*), 2225.
Benzoyloximino-derivatives of hydroxy-2:2:3:3-tetramethyl*cyclo*pentanones (S... PER), 1668.
$C_{23}H_{26}O_4N_2$ Brucine, constitution of (FAWCETT, PERKIN, and ROBINSON), 3082.
$C_{23}H_{27}O_6N$ 6:7:3′:4′-Tetramethoxy-9-methyl-2′-carbomethoxy-3:4-dihydroprot papaverine (*KOEPFLI* and *PERKIN*), 2999.

23 IV

$C_{23}H_{17}O_2N_2Cl$ 3-Phenyl-2-*p*-chlorophenylacetoxymethylquinoxaline (BENNETT an WILLIS), 1974.
$C_{23}H_{16}O_4N_2S$ 1:2-Naphthaquinone 2′-carboxyphenyl sulphoxide phenylhydrazon (*PRICE* and *SMILES*), 3159.
$C_{23}H_{26}O_4N_2S_2$ *pp*′-Ditoluenesulphonyl-αγ-amino-β-phenylpropane (JACKSON an KENNER), 1659.

C_{24} Group.

$C_{24}H_{16}O_5$ Diacetoxy*iso*dinaphthylene oxide (CLEMO and SPENCE), 2817.
$C_{24}H_{14}O_6$ *Diacetoxydinaphthaquinone* (*CLEMO* and *SPENCE*), *2817*.
$C_{24}H_{18}N_2$ 2:3-Distyrylquinoxaline (BENNETT and WILLIS), 1968.
$C_{24}H_{20}O_2$ 4-Phenacyl-3-phenyl-2-methyl-1:4-benzopyran (HILL), 258.
$C_{24}H_{20}Cl_2$ *1:5-Dichloro-9-benzyl-10-isopropylanthracene* (*BARNETT* and *COOK*) 570.
$C_{24}H_{22}O_6$ ω-Benzoyloxy-4-benzyloxy-3:5-dimethoxyacetophenone (BRADLEY an ROBINSON), 1557.
Resorcinolphthalein tetramethyl ether (LUND), 1574.
$C_{24}H_{22}O_{11}$ *Triacetylirigenin* (*BAKER*), *1028*.
$C_{24}H_{26}O_{13}$ Iridin, constitution of (BAKER), 1022.
$C_{24}H_{28}O_{13}$ ω-*O*-Tetra-acetyl-β-glucosidoxy-4-acetoxyacetophenone (ROBERTSON an ROBINSON), 1466.
$C_{24}H_{30}O_3$ Menthyl 2′-methoxydiphenyl-2-carboxylate (BRETSCHER, RULE, an SPENCE), 1502.

24 III

$C_{24}H_{14}O_8N_6$ 2:3-Di(2:4-dinitrostyryl)quinoxaline (BENNETT and WILLIS) 1970.
$C_{24}H_{16}O_4N_4$ 2:3-Di(nitrostyryl)quinoxalines (BENNETT and WILLIS), 1969.
$C_{24}H_{16}N_2Cl_2$ 2:3-Di(chlorostyryl)quinoxalines (BENNETT and WILLIS), 1971.
$C_{24}H_{16}N_2I_2$ 2:3-Di(*o*-iodostyryl)quinoxaline (BENNETT and WILLIS), 1971.
$C_{24}H_{18}N_2Br_4$ 2:3-Distyrylquinoxaline tetrabromide (BENNETT and WILLIS) *1968*.
$C_{24}H_{19}O_8Cl$ 5-Benzoylmalvidin chloride (BRADLEY and ROBINSON), 1561.
$C_{24}H_{21}O_9Al$ Aluminium methyl salicylate (BURROWS and WARK), 228.
$C_{24}H_{25}N_2I$ *Methyldiethyl-ψ-cyanine iodide* (*HAMER*), *212*.
$C_{24}H_{27}N_2I$ 3:3-Dimethyl-1:1′-diethylindo-ψ-cyanine iodide (HAMER), 214.
$C_{24}H_{30}O_4N_4$ 4:4′-Dipiperidino-5:5′-dinitro-3:3′-dimethyldiphenyl (LE FÈVRE an TURNER), 967.

24 IV

$C_{24}H_{16}N_2Cl_2As_2$ 2:2′-Bis(10-chloro-5:10-dihydrophenarsazine) (GIBSON and JOHN SON), 2206.

$C_{24}H_{16}N_2Br_2As_2$ 2:2′-Bis(10-bromo-5:10-dihydrophenarsazine) (GIBSON and JOHNSON), 2210.

$C_{24}H_{18}O_4N_2As_2$ 2:2′-Bis(phenarsazinic acid), and its salts (GIBSON and JOHNSON), 2209.

$C_{24}H_{22}O_4N_2As_2$ 4:4-Bis(diphenylamine-2′-arsinic acid) (GIBSON and JOHNSON), 2208.

$C_{24}H_{23}N_2BrS_2$ 8-Methyl-2:2′-diallylthiocarbocyanine bromide (HAMER), 3162.

C_{25} Group.

$C_{25}H_{20}N_2$ 2:3-Distyryl-6-methylquinoxaline (BENNETT and WILLIS), 1971.

$C_{25}H_{16}O_8$ 2-Benzoyl-1:7-diacetylanthrapurpurin (PERKIN and STOREY), 236.

$C_{25}H_{18}N_2$ Dibenzylidenequinoxalino*cyclo*pentane (BENNETT and WILLIS), 1973.

$C_{25}H_{20}O_5$ 5-Hydroxy-7:4′-dimethoxy-2-styryl*iso*flavone (BAKER and ROBINSON), 3116.

$C_{25}H_{22}Sn$ Triphenylbenzylstannane (KIPPING), 2368.

Triphenyl-*o*-tolylstannane (KIPPING), 2369.

$C_{25}H_{24}O_5$ Dipiperonylidene-3:3:4:4-tetramethyl*cyclo*pentanone (INGOLD and SHOPPEE), 391.

$C_{25}H_{40}O$ Cholesterol, dry distillation of (HEILBRON and SEATON), 347.

25 III

$C_{25}H_{16}O_4N_4$ Di-*p*-nitrobenzylidenequinoxalino*cyclo*pentane (BENNETT and WILLIS), 1973.

$C_{25}H_{16}O_8N_6$ 2:3-Di(2:4-dinitrostyryl)-6-methylquinoxaline (BENNETT and WILLIS), 1972.

$C_{25}H_{18}O_4N_4$ 2:3-Di(*m*-nitrostyryl)-6-methylquinoxaline (BENNETT and WILLIS), 1972.

$C_{25}H_{19}ON$ Diphenyl-2-carboxylylamide (BELL), 3247.

$C_{25}H_{20}O_2N$ 4-Benzylaminomethyl-1-phenyl-3:4-dihydro*iso*quinoline (JACKSON and KENNER), 1660.

$C_{25}H_{21}O_7Cl$ 7-Hydroxy-5-benzoyloxy-3:3′:5′-trimethoxyflavylium chloride (ROBERTSON, ROBINSON, and SUGIURA), 1536.

$C_{25}H_{21}O_8Cl$ 5:7:4′-Trihydroxy-3:3′:5′-trimethoxyflavylium chloride (BRADLEY and ROBINSON), 1567.

$C_{25}H_{21}N_2I$ Dimethylbenz-ψ-cyanine iodide (HAMER), 212.

$C_{25}H_{22}O_4N_2$ Deoxytrimethylbrazilone (PERKIN, RÂY, and ROBINSON), 1508.

$C_{25}H_{22}O_6N_4$ *d*-*a*-1:4-Di-*m*-nitrobenzoyl-2:3:7-trimethyl-1:2:3:4-tetrahydroqninoxaline (GIBSON, NUTLAND, and SIMONSEN), 113.

$C_{25}H_{24}O_3N_2$ 1-Dibenzyl-2-pyrrolidone-5-carboxyanilide (GRAY), 1266.

$C_{25}H_{25}O_3N$ Benzylidenethebainone (GULLAND), 704.

$C_{25}H_{27}O_3N$ Benzylidenethebainol (GULLAND), 706.

Benzylthebainones (GULLAND), 705.

$C_{25}H_{27}O_4N$ Benzylidenehydroxydihydrothebainone (GULLAND), 704.

$C_{25}H_{28}O_3N_2$ Benzylthebainone oxime (GULLAND), 706.

$C_{25}H_{39}O_7N$ Pyropseudaconine (SHARP), 3098.

$C_{25}H_{41}O_8N$ Pseudaconine (HENRY and SHARP), 1112.

25 IV

$C_{25}H_{23}ON_4S$ 3-Phenylmethylmethyleneamino-2:4-diketo-5-phenyltetrahydrothiazole 2-phenylmethylmethylenehydrazone (STEPHEN and WILSON), 1418.

$C_{25}H_{24}O_2N_2S$ *p*-Toluenesulphonyl-*a*-*NN*′-dimethyl-2-phenylnaphthylene-1:3-diamine (GIBSON, KENTISH, and SIMONSEN), 2137.

$C_{25}H_{30}O_4N_2S_2$ *NN'*-Dimethyl-*NN'*-di-*p*-toluenesulphonyl-αγ-diamino-β-phenylpropane (JACKSON and KENNER), 1659.

C_{26} Group.

$C_{26}H_{18}O$ 2-Benzylidene-3-phenyl-Δ³-β-naphthapyran (DICKINSON, HEILBRON, an O'BRIEN), 2081.

$C_{26}H_{20}O_3$ 4-Hydroxytetraphenylmethane-3-carboxylic acid (BOYD and HARDY), 634.

$C_{26}H_{22}O_5$ 5:7:4'-Trimethoxy-2-styryl*iso*flavone (BAKER and ROBINSON), 3116.

$C_{26}H_{24}O_9$ Substance, from deoxytrimethylbrazilone and perbenzoic acid (PERKIN, RÂY, and ROBINSON), 1509.

$C_{26}H_{26}O_8$ Phloroglucinolphthalein hexamethyl ether (LUND), 1573.

$C_{26}H_{28}O_8$ Hexamethoxytriphenylmethane-4-carboxylic acid (LUND), 1572.

26 III

$C_{26}H_{18}OS_2$ Benzildiphenylene-2:2'-mercaptol (BARBER and SMILES), 1147.

$C_{26}H_{18}O_4N_2$ 2:3-Di(methylenedioxystyryl)quinoxaline (BENNETT and WILLIS), 1968.

$C_{26}H_{19}O_3Br$ 5-Bromo-4-hydroxytetraphenylmethane-3-carboxylic acid (BOYD an HARDY), 635.

$C_{26}H_{20}O_4N_6$ Dinitrobenzilosazone (CHATTAWAY and COULSON), 1087, 1363.

$C_{26}H_{20}O_6N_2$ 4:4''-Diethyloxamidodiphenyl (LE FÈVRE and TURNER), 251.

$C_{26}H_{21}O_2N_5$ 4-*Nitrobenzilosazone* (CHATTAWAY and COULSON), 1083.

$C_{26}H_{22}O_2N_2$ 2:3-Di(methoxystyryl)quinoxalines (BENNETT and WILLIS), 1969.

$C_{26}H_{24}O_4N_2$ Dianhydro-6-aminopiperonaldihydrocodeinone (GULLAND), 708.

$C_{26}H_{25}O_5N$ *Piperonylidenethebainone* (GULLAND), 705.

$C_{26}H_{30}O_3N_4$ Benzylthebainone semicarbazones (GULLAND), 705.

$C_{26}H_{31}O_4N$ Diacetylcarvacrylacetonitrile (BELL and HENRY), 2224.
Diacetylthymylacetonitrile (BELL and HENRY), 2224.
Diacetylthymylcarvacrylacetonitrile (BELL and HENRY), 2225.

26 IV

$C_{26}H_{18}O_2N_2Br_2$ 5:4'-Dibromo-3:4-dibenzoylaminodiphenyl (HINKEL and HEY) 1840.

$C_{26}H_{19}NClBr$ 4-Chloro-9-benzylanthracene-ω-pyridinium bromide (COOK), 2809.

$C_{26}H_{20}ON_4Br_2$ *Azoxybenzylidene-p-bromoanilines* (NISBET), 3123.

$C_{26}H_{20}O_2N_2S_2$ 2:2'-Dibenzamidodiphenyl disulphide (CLARK), 2320.

$C_{26}H_{20}N_2Cl_2As_2$ 2:2'-Bis(10-chloro-8-methyl-5:10-dihydrophenarsazine) (GIBSON an JOHNSON), 2210.

$C_{26}H_{20}N_2Br_2As_2$ 2:2'-Bis(10-bromo-8-methyl-5:10-dihydrophenarsazine) (GIBSO and JOHNSON), 2211.

$C_{26}H_{20}N_2I_2As_2$ 2:2'-Bis(10-iodo-8-methyl-5:10-dihydrophenarsazine) (GIBSON an JOHNSON), 2211.

$C_{26}H_{22}O_4N_2As_2$ *2:2'-Bis(8-methylphenarsazinic acid), and its sodium salt* (GIBSO and JOHNSON), 2210.

$C_{26}H_{28}O_3NI$ Benzylidenethebainone methiodide (GULLAND), 705.

C_{27} Group.

$C_{27}H_{20}$ 9:9-Diphenyl-10-methylene-9:10-dihydroanthracene (BARNETT and COOK), 570.

$C_{27}H_{44}$ ψ-Cholestene, formation of, from dry distillation of cholesterol (HEILBRO and SEXTON), 347.

27 II

$C_{27}H_{22}O_6$ 5-Acetoxy-7:4′-dimethoxy-2-styryl*iso*flavone (BAKER and ROBINSON), 3116.

$C_{27}H_{22}O_{14}$ Hexa-acetylirigenol (BAKER), 1030.

$C_{27}H_{24}O$ 4-Methoxy-3-methyltetraphenylmethane (BOYD and HARDY), 637.

$C_{27}H_{24}O_5$ 5:7:4′-Trimethoxy-2-styryl-6-methyl*iso*flavone (BAKER and ROBINSON), 3117.

$C_{27}H_{26}Sn$ Phenyldi-*p*-tolylbenzylstannane (KIPPING), 2370.
Phenyltribenzylstannane (KIPPING), 2367.

$C_{27}H_{32}O_2$ *m*-Hydroxyphenyldithymylmethane (BELL and HENRY), 2226.

$C_{27}H_{42}O_2$ Campnospermonol (JONES and SMITH), 65.

$C_{27}H_{44}O$ Cholestenone, preparation of (SEXTON), 2825.

27 III

$C_{27}H_{17}Cl_2Br$ ω-Bromo-1:5-dichloro-9-benzyl-10-phenylanthracene (COOK), 2805.

$C_{27}H_{18}OCl_2$ ω-Hydroxy-1:5-dichloro-9-benzyl-10-phenylanthracene (COOK), 2805.

$C_{27}H_{20}OCl_2$ 1:5-Dichloro-10-phenyl-9-benzyl-9:10-dihydroanthranol (BARNETT and COOK), 569.

$C_{27}H_{20}O_4N_2$ 2:3-Di(methylenedioxystyryl)-6-methylquinoxaline (BENNETT and WILLIS), 1971.

$C_{27}H_{21}ON$ Benzoyl-1:3-diphenyldihydro*iso*indole (BOYD and LADHAMS), 2093.

$C_{27}H_{23}OBr$ 3-Bromo-4-methoxy-5-methyltetraphenylmethane (BOYD and HARDY), 638.

$C_{27}H_{24}O_2N_2$ 2:3-Di(*p*-methoxystyryl)-6-methylquinoxaline (BENNETT and WILLIS), 1971.

$C_{27}H_{25}N_2I$ Diethylbenz-ψ-cyanine iodide (HAMER), 212.

$C_{27}H_{27}O_9Al$ Aluminium ethyl salicylate (BURROWS and WARK), 228.

$C_{27}H_{30}O_6N_2$ αγ-Dibenzoylamino-β-3:4-dibenzoyloxyphenylpropane (JACKSON and KENNER), 1662.

$C_{27}H_{31}O_2Cl$ Chlorophenyldithymylmethanes (BELL and HENRY), 2226.

$C_{27}H_{31}O_4N$ Nitrophenyldithymylmethanes (BELL and HENRY), 2226.

27 IV

$C_{27}H_{27}O_4N_2I$ Dianhydro-6-aminopiperonaldihydrocodeinone methiodide (GULLAND), 703.

C_{28} Group.

$C_{28}H_{20}Cl_2$ 1:5-Dichloro-9-benzyl-10-benzylidene-9:10-dihydroanthracene (BARNETT and COOK), 570.

$C_{28}H_{22}O_4$ 4-Acetoxytetraphenylmethane-3-carboxylic acid (BOYD and HARDY), 635.

$C_{28}H_{24}O_2$ 4-Acetoxy-3-methyltetraphenylmethane (BOYD and HARDY), 637.

$C_{28}H_{28}Si$ Tetrabenzylsilicane, preparation of (STEELE and KIPPING), 1431.

$C_{28}H_{28}Sn$ Tritolyltolylstannanes (KIPPING), 2369.

$C_{28}H_{34}O_8$ Ethyl βγ-diphenylbutane-ααδδ-tetracarboxylates (VOGEL), 1019.

$C_{28}H_{46}O$ Substance, from reduction of campnospermonyl methyl ether (JONES and SMITH), 69.

$C_{28}H_{46}O_2$ Substance, from reduction of campnospermonol (JONES and SMITH), 69.

$C_{28}H_{48}O_2$ Hydrocampnospermonyl methyl ether (JONES and SMITH), 69.

$C_{28}H_{50}O$ Substance, from reduction of campnospermonyl methyl ether (JONES and SMITH), 69.

28 III

$C_{28}H_{21}OCl$ 1-Chloro-10:10-dibenzylanthrone (BARNETT and COOK), 572.

$C_{28}H_{22}OCl_2$ 1:5-Dichloro-9:10-dibenzyl-9:10-dihydroanthranol (BARNETT and COOK), 569.

$C_{28}H_{24}ON_4$ *m*-Azoxybenzylidene-*p*-toluidine (NISBET), 3124.

$C_{28}H_{24}O_2S_2$ Benzil benzyl mercaptol dioxide (CHIVERS and SMILES), 699.

$C_{28}H_{26}O_4N_2$ 2:3-Di(3:4-dimethoxystyryl)quinoxaline (BENNETT and WILLIS), 1969.

$C_{28}H_{27}O_3N_3$ 4-Anilino-3-*o*-carbethoxyphenylmethylcarbamyl-1-methyl-2-methylene-1:2-dihydroquinoline (HEILBRON, HOLT, and KITCHEN), 989.

$C_{28}H_{32}O_8Br$ Ethyl *r*-αδ-dibromo-βγ-diphenylbutane ααδδ-tetracarboxylate (VOGEL), 1020.

$C_{28}H_{49}O_2N$ Hydrocampnospermonyl methyl ether oxime (JONES and SMITH), 69.

C_{29} Group.

$C_{29}H_{20}O_2$ 3:3′-Diphenyldibenzo*spiro*pyran (DICKINSON, HEILBRON, and O'BRIEN), 2081.

$C_{29}H_{26}O$ 9:9-Dibenzyl-10-methyl-9:10-dihydroanthranol (BARNETT and COOK), 571.

$C_{29}H_{30}O_{13}$ ω-*O*-Tetra-acetyl-β-glucosidoxy-4-benzoyloxyacetophenone (ROBERTSON and ROBINSON), 1466.

$C_{29}H_{46}O_2$ Campnospermonyl methyl ether (JONES and SMITH), 67.

29 III

$C_{29}H_{22}OCl_2$ ω-Ethoxy-1:5-dichloro-9-benzyl-10-phenylanthracene (COOK), 2805.

$C_{29}H_{22}O_3N_2$ Dibenzoyl derivative of substance $C_{15}H_{14}ON_2$ (KRISHNAMURTI), 416.

$C_{29}H_{28}O_4N_2$ 2:3-Di(3:4-dimethoxystyryl)-6-methylquinoxaline (BENNETT and WILLIS), 1971.

$C_{29}H_{32}ON_2$ *NN′*-Dimethyl-2-phenylnaphthylene-1:8-diamino-*d*-methylenecamphor (GIBSON, KENTISH, and SIMONSEN), 2137.

$C_{29}H_{47}O_2N$ Campnospermonyl methyl ether oxime (JONES and SMITH), 67.

C_{30} Group.

$C_{30}H_{26}O$ Bis-αγ-diphenylallyl ether (SHOPPEE), 2570.
Bis-αγ-diphenylpropenyl ether (SHOPPEE), 2570.

30 III

$C_{30}H_{22}O_6Mo$ Molybdyl bisdibenzoylmethane (MORGAN and CASTELL), 3255.

$C_{30}H_{24}OBr_2$ Bis-β-bromo-αγ-diphenylpropenyl ether (SHOPPEE), 2570.

$C_{30}H_{24}O_2N_2$ *NN′*-Dicinnamoylbenzidine (LE FÈVRE and TURNER), 252.

$C_{30}H_{24}O_3N_2$ Dibenzoyl derivative of substance $C_{16}H_{16}ON_2$ (KRISHNAMURTI), 416.

$C_{30}H_{26}OBr_2$ Bis-βγ-dibromo-αγ-diphenylpropyl ether (SHOPPEE), 2570.

$C_{30}H_{26}O_4N_2$ αγ-Dibenzoylamino-β-*p*-benzoyloxyphenylpropane (JACKSON and KENNER), 1661.

$C_{30}H_{27}O_3N_5$ Diketosuccinodibenzylamic acid phenylosazone (CHATTAWAY and HUMPHREY), 1097.

$C_{30}H_{31}O_8P$ Bis-αγ-diphenoxy*iso*propyl phosphate (BOYD and LADHAMS), 220.

30 IV

$C_{30}H_{26}O_4N_2S_2$ Di-*p*-toluenesulphonyl-2-phenylnaphthylene-1:3-diamines (GIBSON, KENTISH, and SIMONSEN), 2138.

$C_{30}H_{25}O_6N_4S_3$ Diphenylamine-2:4:6-trisulphonanilide (DAVIES and WOOD), 1125.

C_{31} Group.

$C_{31}H_{40}O_3$ Trithymylmethane (BELL and HENRY), 2223.

31 III

$C_{31}H_{43}O_{10}N$ Triacetylpyropseudaconine (SHARP), 3099.

C_{32} Group.

$_{32}H_{24}O_{10}$ 7:3′-Dibenzoylirigenin (BAKER), 1028.

32 III

$_{32}H_{34}O_{6}N_{2}$ NN′-Di-o-carbethoxybenzoylbenzidine (LE FÈVRE and TURNER), 251.

$_{32}H_{28}O_{2}N_{4}$ 4-Anilino-3-o-anilinophenylmethylcarbamyl-1-methyl-2-methylene-1:2-dihydroquinoline (HEILBRON, HOLT, and KITCHEN), 940.

$_{32}H_{32}O_{2}N_{6}$ Benzildi-d-δ-(α-phenylethyl)semicarbazone (HOPPER and WILSON), 2488.

$_{32}H_{49}O_{11}N$ Triacetylmethylpseudaconine (SHARP), 3102.

32 IV

$_{32}H_{30}O_{4}N_{2}S_{2}$ Di-p-toluenesulphonyl-NN′-dimethyl-2-phenylnaphthylene-1:3-diamine (GIBSON, KENTISH, and SIMONSEN), 2139.

C_{33} Group.

$_{33}H_{24}$ 9:9-Diphenyl-10-benzylidene-9:10-dihydroanthracene (BARNETT and COOK), 571.

33 II

$_{33}H_{26}O$ 9:9-Diphenyl-10-benzyl-9:10-dihydroanthranol (BARNETT and COOK), 571.

33 III

$_{33}H_{29}O_{3}P$ Di-p-tolyl triphenylmethylphosphite (BOYD and HARDY), 636.

$_{33}H_{40}O_{18}N_{4}$ Substance, from oxidation of pseudaconitine (HENRY and SHARP), 1113.

$_{33}H_{48}O_{4}N_{2}$ 4-Hydroxy-3-aldehydo-5-methyl-2-isopropylphenyldicarvacrylmethane (BELL and HENRY), 2221.

$_{33}H_{49}O_{12}N$ Tetra-acetylpseudaconine (HENRY and SHARP), 1112.

$_{33}H_{51}O_{11}N$ Triacetylethylpseudaconine (SHARP), 3102.

C_{34} Group.

$_{34}H_{28}O$ 10-Phenyl-9:9-dibenzyl-9:10-dihydroanthranol (BARNETT and COOK), 571.

34 III

$_{34}H_{27}OCl$ 1-Chloro-9-phenyl-10:10-dibenzyl-9:10-dihydroanthranol-9 (BARNETT and COOK), 572.

$_{34}H_{31}N_{2}Br_{2}$ Neocyanine methobromide (HAMER), 1477.

$_{34}H_{37}O_{7}N$ Demethylpyropseudaconine (SHARP), 3099.

$_{34}H_{39}O_{8}P$ Bis-αγ-di-p-tolyloxyisopropyl phosphate (BOYD and LADHAMS), 219.

$_{34}H_{42}O_{17}N_{2}$ Substance, from oxidation of pseudaconitine (HENRY and SHARP), 1117.

$_{34}H_{45}O_{11}N$ Substance, and its salts, from oxidation of pseudaconitine (HENRY and SHARP), 1117.

$_{34}H_{47}O_{10}N$ Pyropseudaconitine (SHARP), 3097.

C_{35} Group.

$_{35}H_{50}O_{6}N_{2}$ Batyl p-nitrobenzoate (HEILBRON and OWENS), 944.

$_{35}H_{51}O_{11}N$ Veratroylmethylpseudaconine, and its salts (SHARP), 3100.

$_{35}H_{54}O_{5}N_{2}$ Batyl phenylurethane (HEILBRON and OWENS), 944.

C_{36} Group.

[illegible] 9:9:10-Tribenzyl-9:10-dihydroanthranol (BARNETT and COOK), 571.

36 III

$C_{36}H_{26}O_5N_2$ 2-Azoxystyryl-3-methylchromones (NISBET), 3123.

$C_{36}H_{30}O_7Se_2$ Tri-4-hydroxytriphenylselenonium oxide (MORGAN and BURSTAL 3265.

$C_{36}H_{50}O_2Cl_2$ Bis-(4-chlorostyryl nonyl ketone) (HEILBRON and IRVING), 2326.

$C_{36}H_{51}O_{12}N$ Pseudaconitine (SHARP), 3094; and its salts (HENRY and SHAR 1111.

$C_{36}H_{53}O_2N$ Bis(styryl nonyl ketone) oxime (HEILBRON and IRVING), 2324.

36 IV

$C_{36}H_{32}O_{17}S_3Se_3$ Triphenoxselenylium dibisulphate sulphuric acid dihydr (DREW), 523.

36 V

$C_{36}H_{30}O_6Cl_6Se_2Pb$ Tri-4-hydroxytriphenylselenonium chloroplatinate (MORG and BURSTALL), 3265.

C_{37} Group.

$C_{37}H_{24}O_2$ 3:3′-Diphenyldi-β-naphtha*spiro*pyran (DICKINSON, HEILBRON, a O'BRIEN), 2082.

$C_{37}H_{24}O_9$ *O*-Tribenzoylbrazilone (PERKIN, RÂY, and ROBINSON), 1513.

$C_{37}H_{46}O_6$ Triacetylcarvacrylmethane (BELL and HENRY), 2223.
Triacetylthymylmethane (BELL and HENRY), 2223.

37 III

$C_{37}H_{37}N_3Br_2$ Neocyanine ethobromide (HAMER), 1477.

$C_{37}H_{37}N_3I_2$ Neocyanine ethiodide (HAMER), 1476.

$C_{37}H_{45}O_{17}N_3$ Acetyl derivative of substance $C_{33}H_{40}O_{16}N$ (HENRY and SHAR 1114.

$C_{37}H_{53}O_{12}N$ Acetylveratroylmethylpseudaconine, and its perchlorate (SHAR 3101.

37 IV

$C_{37}H_{32}O_6N_2S_3$ Tri-*p*-toluenesulphonyl-2-phenylnaphthylene-1:3-diamine (GIBSO *KENTISH, and SIMONSEN*), 2139.

C_{38} Group.

$C_{38}H_{52}O_6$ Bis-(3:4-methylenedioxystyryl nonyl ketone) (HEILBRON and IRVIN 2325.

$C_{38}H_{56}O_2$ Bis-(4-methylstyryl nonyl ketone) (HEILBRON and IRVING), 2325.

$C_{38}H_{56}O_4$ Bis-(4-methoxystyryl nonyl ketone) (HEILBRON and IRVING), 2324.

38 III

$C_{38}H_{35}O_{11}Cl$ 3-*O*-Tetra-acetyl-β-glucosidoxy-7-hydroxy-5-benzoyloxy-4′-acetoxy-flavylium chloride (ROBERTSON and ROBINSON), 1467.

$C_{38}H_{53}O_{13}N$ Acetylpseudaconitine, and its perchlorate (SHARP), 3105.

C_{39} Group.

$C_{39}H_{51}O_{13}N$ Triacetyldemethylpyropseudaconitine (SHARP), 3098.

$C_{39}H_{55}O_{13}N$ Diacetylveratroylmethylpseudaconine (SHARP), 3102.

C_{40} Group.

$C_{40}H_{40}O_{12}$ Ethyl di(*O*-benzyl syringoylsuccinate) (BRADLEY and ROBINSON), 15

$C_{40}H_{60}O_6$ Bis-(3:4-dimethoxystyryl nonyl ketone) (HEILBRON and IRVING), 232

40 III

$C_{40}H_{55}O_{14}N$ Diacetylpseudaconitine (SHARP), 3105.

C_{42} Group.

$C_{42}H_{64}O_2$ Bis-(4-*iso*propylstyryl nonyl ketone) (HEILBRON and IRVING), 2325.

42 III

$C_{42}H_{42}OSi_2$ Tetrabenzylsilicyl oxide, preparation of (STEELE and KIPPING), 1431.

$C_{42}H_{42}O_7Se_3$ Trihydroxytrimethyltriphenylselenonium oxides (MORGAN and BURSTALL), 3266.

C_{44} Group.

$C_{44}H_{42}O_6N_4ClI$ 4′-Chloro-3:3′-di(*o*-carbethoxyphenylmethylcarbamyl)-1:2:1′-trimethyl*iso*cyanine iodide (HEILBRON, HOLT, and KITCHEN), 940.

C_{45} Group.

$C_{45}H_{55}O_{13}N$ Benzoylpseudaconitine, and its perchlorate (SHARP), 3104.

C_{57} Group.

$C_{57}H_{104}O_5$ Triolein, heating of, with sulphur (KNIGHT and STAMBERGER), 2791.

ERRATA.

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Page	Line	
2050	5*	*for* "$[\alpha]_D^{20°} - 250°$" *read* "$[\alpha]_D^{20°} + 116{\cdot}1°$."

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371	1*	*for* "sink" *read* "source."
605	20	*for* "Holleman and de Bruyn, *Rec. trav. chim.*, 1900, **19**, 79" *read* "Baker and Wilson, J., 1927, 842."
607	footnote	*for* "unsuitable solvent" *read* "unsuitable quantity of solvent."
850	1	for "S^2V^2/M^2n^2" read "S^2V^2/Mn^2."
857	10	for "s" read "s^2."
861	Fig. 1	The axis of abscissæ is the longer axis on the right.
863	1	for "x" read "X."
865	17	for "$(M + m, V + m, E - \epsilon')$" read "$(M - m', V + m', E - \epsilon')$."
865	19	for "x" read "x'."
867	Fig. 3	The axis of abscissæ is the longer axis on the right.
871	15	*for* "sech $(U - u)$" *read* "sech $(U - u')$."
871	16	*for* "tanh $(U - u)$" *read* "tanh $(U - u')$."
872	6, 22	*after* "Table I" *insert* "(Part I)."
1585	first formula	*for* "$\overset{\ominus}{H}$ + HO −" *read* "$\overset{\ominus}{OH}$ + H −."
2485	7*	*for* "m. p. 187°" *read* "m. p. 137°."
	*	*for* "Martins" *read* "Martius."

* From bottom.